

Vol. 24, No. 4, July-August, 1989

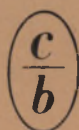
March, 1990

LITHOLOGY AND MINERAL RESOURCES

ЛИТОЛОГИЯ И ПОЛЕЗНЫЕ ИСКОПАЕМЫЕ

(LITOLOGIYA I POLEZNYE ISKOPAEMYE)

TRANSLATED FROM RUSSIAN



CONSULTANTS BUREAU, NEW YORK

LITHOLOGY AND MINERAL RESOURCES

Lithology and Mineral Resources is abstracted or indexed in *Chemical Abstracts*, *Engineering Index*, and *Metal Abstracts Index*.

Lithology and Mineral Resources is a translation of *Litologiya i Poleznye Iskopaemye*, a publication of the Academy of Sciences of the USSR.

An agreement with the Copyright Agency of the USSR (VAAP) makes available both advance copies of the Russian journal and original glossy photographs and artwork. This serves to decrease the necessary time lag between publication of the original and publication of the translation and helps to improve the quality of the latter. The translation began with the first issue of the Russian journal.

Editorial Board of *Litologiya i Poleznye Iskopaemye*:

Editor: V. N. Kholodov

Associate Editors: B. M. Mikhailov and P. P. Timofeev

Secretary: G. Yu. Butuzova

A. N. Dmitrievskii

A. V. Il'in

V. I. Kononov

A. I. Konyukhov

A. A. Migdisov

I. O. Murdmaa

V. I. Sedletskii

E. M. Shmarinovich

E. F. Shnyukov

S. A. Sidorenko

I. I. Volkov

O. V. Yapaskurt

Copyright ©1990, Plenum Publishing Corporation. *Lithology and Mineral Resources* participates in the Copyright Clearance Center (CCC) Transactional Reporting Service. The appearance of a code line at the bottom of the first page of an article in this journal indicates the copyright owner's consent that copies of the article may be made for personal or internal use. However, this consent is given on the condition that the copier pay the flat fee of \$12.50 per article (no additional per-page fees) directly to the Copyright Clearance Center, Inc., 27 Congress Street, Salem, Massachusetts 01970, for all copying not explicitly permitted by Sections 107 or 108 of the U.S. Copyright Law. The CCC is a nonprofit clearinghouse for the payment of photocopying fees by libraries and other users registered with the CCC. Therefore, this consent does not extend to other kinds of copying, such as copying for general distribution, for advertising or promotional purposes, for creating new collective works, or for resale, nor to the reprinting of figures, tables, and text excerpts. 0024-4902 /89/\$12.50

Consultants Bureau journals appear about six months after the publication of the original Russian issue. For bibliographic accuracy, the English issue published by Consultants Bureau carries the same number and date as the original Russian from which it was translated. For example, a Russian issue published in December will appear in a Consultants Bureau English translation about the following June, but the translation issue will carry the December date. When ordering any volume or particular issue of a Consultants Bureau journal, please specify the date and, where applicable, the volume and issue numbers of the original Russian. The material you will receive will be a translation of that Russian volume or issue.

Subscription (6 Issues)

Vol. 23: \$795 (domestic); \$880 (foreign)

Single Issue: \$150

Vol. 24: \$855 (domestic); \$990 (foreign);

Single Article: \$12.50

CONSULTANTS BUREAU, NEW YORK AND LONDON



233 Spring Street
New York, New York 10013

Published bimonthly, consisting of Volume 23 issues 3 through 6 and Volume 24 issues 1 and 2. Subscription price for Volume 23 is \$795, and for Volume 24 is \$855. Second-class postage paid at Jamaica, New York 11431.

Mailed in the USA by Publications Expediting, Inc., 200 Meacham Avenue, Elmont, NY 11003.

POSTMASTER: Send address changes to *Lithology and Mineral Resources*, Plenum Publishing Corporation, 233 Spring Street, New York, NY 10013.

LITHOLOGY AND MINERAL RESOURCES

A translation of *Litologiya i Poleznye Iskopaemye*

March, 1990

Volume 24, Number 4

July-August, 1989

CONTENTS

Engl./Russ.

Sedimentation Features in the Indonesian Geosynclinal Region. Report 2. Late Cenozoic and Recent Marine Deposits and Their Formation Conditions - I. V. Khvorova.....	309	3
Differences between Birnessites of Sedimentary and Hydrothermal Origin - L. E. Shterenberg, V. A. Drits, A. L. Salyn', and N. L. Kalashnikova.....	320	17
Ferromanganese Crusts and Nodules in the Kurile Island Arc: Structure, Composition, and Origin - T. Yu. Uspenskaya, A. I. Gorshkov, G. M. Gavrilenko, and A. V. Sivtsov.....	330	30
Postdepositional Injected-Convolute Phosphorites of the Far East - V. A. Nagorny.....	339	41
Physical-Chemical Settings of Uranylvanadate Ore Formation - I. G. Zhil'tsova, S. A. Perlina, and E. M. Shmariovich.....	350	54
An Analysis of Patterns of Post-Sedimentational Formation of Pliocene-Quaternary Deposits of the Baku Archipelago on the Basis of a Factor Model - A. S. Polyakov and B. A. Shmagin.....	356	61
The Problem of the Interrelationships between Vitrinite Reflectance and the Lithological Characteristics of Sedimentary Rocks - A. N. Fomin.....	367	74
Glauconite Formation Conditions during the Paleogene in the Eastern Mediterranean Based on Isotopic Data - B. G. Pokrovskii and D. I. Golovin.....	375	84
Association of Chlorine-Calcium Solutions with Metasomatic Dolomitization of Limestone - V. G. Popov.....	386	97
Presentation of Mathematical Problems in Reference Books Issued by Nedra Publishers - A. B. Vistelius.....	392	104
METHODS		
Methodology of Radiographic Investigations into the Structure of Subaqueous Sediments - V. M. Voskoboynikov and B. I. Krakovskii.....	402	131

*The Russian press date (podpisano k pechaty) of this issue was 1/24/1990.
Publication therefore did not occur prior to this date, but must be assumed
to have taken place reasonably soon thereafter.*

SEDIMENTATION FEATURES IN THE INDONESIAN GEOSYNCLINAL REGION.

REPORT 2. LATE CENOZOIC AND RECENT MARINE DEPOSITS AND THEIR FORMATION CONDITIONS

I. V. Khvorova

UDC 551.7.022:551.79(9/0)

The characteristics of facies complexes of marine deposits developed in various structural-morphological zones of the Indonesian geosynclinal region is given based on a large amount of literature material. Features of the complexes composition and structure are considered defined by the character of their source provinces and their physical-geographical environment. The great role of gravitational processes and bottom currents in the formation of sedimentary sequences is shown.

In the first report [1] data are cited on the basic features of the geology of the Indonesian geosynclinal region and the characteristics of its basic structural-morphological elements are given. Destructive and constructive processes created here a complex mosaic of great and small islands, underwater uplifts, deep water trenches and seas. The relief of the region is extremely varied: vast, rather flat expanses are connected with areas of extreme relief contrasts, where individual ridge peaks reach 3.5-4 km, and the basin floor is locally found at depths of 5-7 km below sea level. This entire system forms a wide (~4000 km) bridge between two continents, with two sides bounded by oceans.

Recent and late Cenozoic sediment accumulation is defined by the preexisting relief, the composition of the source provinces, and volcanism; the general climatic environment also influences the sedimentation. Deposits here are both terrigenous and marine (shallow and deep water). This article does not consider the first, but it is necessary to keep in mind that in ancient fold regions terrigenous facies are not excluded in the appropriate stage of geosynclinal development.

The marine deposits encompass a large set of material and genetic sediment types, forming characteristic associations or facies complexes. We will consider the most widely distributed of these.

Terrigenous Near-Continental Deposits. They are formed from material carried out from the continent by rivers and redistributed in a shallow water environment by usual marine hydrodynamics (waves and currents). Recent sediments of the complex are primarily represented by greenish silty clays with small quantities of sand, but in periods of glacial-eustatic events sand accumulations were widely distributed. Deposits of the complex are developed in epicontinental seas, on near-delta shelves, and in bays.

The Zondian shelf and Java sea relate to the first. Depths are not predominantly great here (40-80 m), but at the upper shelf edge they reach 150-200 m. The basement relief is uneven, with the graben-like depressions and uplifts characteristic of continental borderlands; however the structural irregularities are smoothed to a significant degree by sediment accumulation [9]. Relict sands are revealed on uplifts and at shelf edges.

The composition of terrigenous material is determined by the two main source provinces [7]. On the greater part of the Asiatic shelf the detrital fraction is represented by quartz, feldspars, and limestones, with an admixture of other minerals, and clay-illite and chlorite; there is much kaolinite (20%) apparent close to the mouth of the Mekong river. Longshore currents of southern direction were of great importance in sediment distribution. The other material source was Sumatra. The clastics are enriched here by a volcanogenic component (dark minerals, plagioclases, rock fragments), while clay is represented by smectites, mixed layered minerals and kaolinite.

Geological Institute, Academy of Sciences of the USSR, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 4, pp. 3-16, July-August, 1989. Original article submitted September 12, 1988.

Foraminifera occur almost universally in the sands; thin-valved bivalves reside on the muddy gulf floors, while thick shelled mollusks are found on the floor of the open shelf. The content of CaCO_3 in the sediments is from 0 to 30%; the high values are found in the middle part of the shelf. Glauconite often occurs.

Seismic profiles yield representation of the structure of the overall sedimentary cover. The discontinuity of reflecting horizons apparent on them denotes structure from turbidite sequences. The Pleistocene lowering of sea level is also sharply expressed on the seismic profiles in the form of remnants of multiple river valleys [8].

Near-delta portions (delta-shelf) of several trough seas are the second ranked developments of the considered deposits. Such deposits are well studied in the Andaman sea [19]. Several rivers enter it on the north, the largest of which is the Irrawaddy river, the greatest source of sedimentary material. It has a great underwater delta, extending across the entire shelf (from 170 to 300 km wide), with a very slight slope toward the seaward side. A system of channel is weakly expressed on the shelf. They open into canyons arranged on the continental slope. The predominating sediments of the delta and shelf are homogeneous, almost non-carbonate silty clays with an insignificant admixture of sand; all of the sand brought by the rivers is deposited on the beach and in near-mouth bars. A few small accumulations of shelly detritus are noted close to shores; evidently the abundant sediment input inhibited faunal development. The sedimentation rate on the shelf is estimated at 200 cm/thousand years (the first level of avalanche sedimentation). On the outer part of the shelf, clay sediments are sharply succeeded by rather coarse feldspar-quartz relict sands with shelly detritus (up to 30%).

Thus, fine, essentially clay, weakly or noncarbonate greenish sediments are characteristic for the near-continental portions of trough (marginal) seas, as well as wide basin shelves (Zondian shelf).

A special variety of the considered deposits are the deposits of shallow water straits. The strait of Malacca, uniting the Zondian shelf and the Andaman sea, serves as an example [14]. The strait is 64 km wide on the east (there are many islands in it here), while on the northwest it is approximately 260 km. Its depth is 27-37 m in the middle. Along the strait there is a current with a velocity reaching 55-103 cm/sec, and 180 cm/sec in narrow interisland "channels". To a significant degree the current determines the microrelief of the floor and the distribution of recent sediments, which various rivers carried out from Sumatra and the Malaccan peninsula. In areas of rapid current, the floor is complicated by transverse sand banks from 4.5 to 15 m high and from 240 to 900 m long; other areas are covered by small ripple marks ($h = 3-4$ cm) oriented parallel to the strait. Uneven sediment distribution is characteristic. Greenish-grey and alive argillaceous fine grained sands and sandy clays predominate overall, but in the olive part gravelly sands with crushed mussels washed from finer fractions are developed over significant areas. As a rule, the CaCO_3 content is low (0-17%), only in individual cases reaching 70%. Carbonate material is represented by the shells of mollusks and foraminifera. The composition of the terrigenous detrital fraction varies somewhat from place to place dependent on the river input. On the whole, quartz dominates and orthoclase generally predominates over plagioclases, although the inverse relation is locally observed; there is sometimes more (up to 25%) volcanic glass and biotite.

The clay fraction is polymineralic and represented by kaolinite, montmorillonite, mixed layered minerals, and illite; there is little chlorite, kaolinite is particularly abundant along the coast of Sumatra, connected with the wide development of laterite weathering crusts. Glauconite is abundant, and its content varies from traces to 80%; pyrite is often noted.

Recent clay-sand sediments lie on hard grey silty clays with abundant plant detritus and scarce finds of glauconite and shelly material; peaty remnants occur locally. It is thought that such deposits are related to the late Pleistocene, when a swampy plane existed in the place of the Malaccan strait [14].

Terrigenous-Carbonate and Carbonate Shallow Water-Marine Deposits. They are represented by two facies types.

Laminated organogenic limestones, sometimes with an admixture of terrigenous and volcanoterrigenous material, relate to the first facies type. The limestones are formed by the skeletal remnants of various marine invertebrates (benthos) and algae, often in the form of detritus, sometimes rounded (skeletal sands). Gravelly varieties alternate with more finely detrital types, determined by the hydrodynamic sorting of the sediment. Such deposits are

characteristic for wide near-island shelves, where rivers do not input suspended material (in noticeable quantities). Many shelves of the Sulu sea fall into this category (Fig. 1). Sediments in its limits are locally almost completely composed of skeletal fragments. Lithologic investigations over a profile from the shelf to the deep sea were conducted here. On the shelf, the content of the carbonate sand fraction reaches 90-100% of the sediment, while at a depth of 760 m it is already only 10% (below 2 km this fraction increases to 28% due to planktonic foraminifera). The composition of shelly material also varies in the same fashion. Benthonic foraminifera form nearly 10% of the sediment on the shelf, while they comprise 2% in the deep water silts; other remnants (algae, mollusks, echinoderms, bryozoans) are the main sediment forming component on the shelf (> 60%), while at a depth of 1200 m they are less than 7%. On the other hand, planktonic foraminifera make up <10% on the shelf, while they make up 70% at a depth of 760 m, and 97% at 1500 m. On the shelf there is a persistent but small quantity of siliceous sponges, insignificant content of diatomic algae, and practically no radiolaria; glauconite occurs, and coral-algal bioherms and portions of solid ground "purified" of sediment by waves and currents occur locally among skeletal sands and gravels.

The second facies type is represented by reefs, which are widely distributed in Indonesia. Fringing reefs and atolls predominate; many have lagoons with mangroves. The main reef builders are corals and algae (lithothamnium predominate); various marine invertebrates (reef-lovers) are abundant here. Their remnants, generally in detrital form, become a significant sediment forming component. Biohermic structures with atypical composition up to 50 m high are detected in the Java sea on the carbonate "platform" (k-bank) [18]. They are formed by the Halimeda algae, and their structure stands out well on seismic profiles; individual biohermic bodies merge together, forming ridges and hilly surfaces on the bank edge. Absence of corals is characteristic here, and there is an unusually large rate (for Halimeda) of biohermic formation (up to 590 cm/1000 years). This is explained by the bank's position close to the Macassar strait, where the thermocline is found at a depth of only 50-100 m. Here cold near-bottom waters (15°C at a depth of 150 m) enter the bank and create local upwelling, which stimulates the high productivity of the Halimeda; evidently the absence of corals is also explained by the temperature regime.

The reef slopes are often steep, even overhanging. This assists the formation of coarsely detrital material. Skeletal sands are formed on the reef plateau. They often form shoals, small accumulative islands, and banks encircling lagoons; the reef peripheries are bordered by limestone pebbles and rubble.

One of the reef features is the very early lithification of many sediments. This is connected with the solution and reprecipitation of calcium carbonate; as a result it is possible to develop solid recrystallized rock in which the primary organogenic structure has vanished; such processes are particularly apparent in beach and littoral sands.

Extinct and active volcanoes of island arc archipelagoes, as well as structural uplifts both in the region of the Zondian shelf and Java sea, and in the limits of buried minicontinents (Spratly, Sisha, etc) all serve as bases for reef complexes. Some reefs have a thickness greater than 550 m [16].

Deposits connected with the active island arc portions of Indonesia are by far the most varied and complex in their formation conditions. Among them it is possible to distinguish the following.

Blocky Mixtites. They are represented by two genetic types: gravitational accumulations and products of volcanic-mud activity.

The first include formations of underwater creep (olistostromes) and pastelike flows (debrites). They are composed of chaotically arranged coarse fragments (to gravel size and larger blocks), included in a relatively finely detrital friable mass (from gravel-sand to silt-clay, sometimes with ash). Coarse fragments fell into the sediments both in the form of solid and weakly lithified rocks; the destruction of the latter during creep formed the connecting mass to a significant degree. Terrigenous rocks play a great and sometimes exclusive role in the clastic composition: massive sands, sand-clay detached masses, and seldom conglomerates and argillites. There are fewer fragments of flints, marls, limestones. Ophiolites, basalts, and metamorphites occur often, but not universally. The mixtite thickness is greater (100-200 m); they generally lie on the dislocated terrigenous rocks comprising the trench's inner slope and its slope foot. A transition to mixtites in turbidite fans was observed [12]. Gravitational creep of such scale has occurred spasmodically throughout long

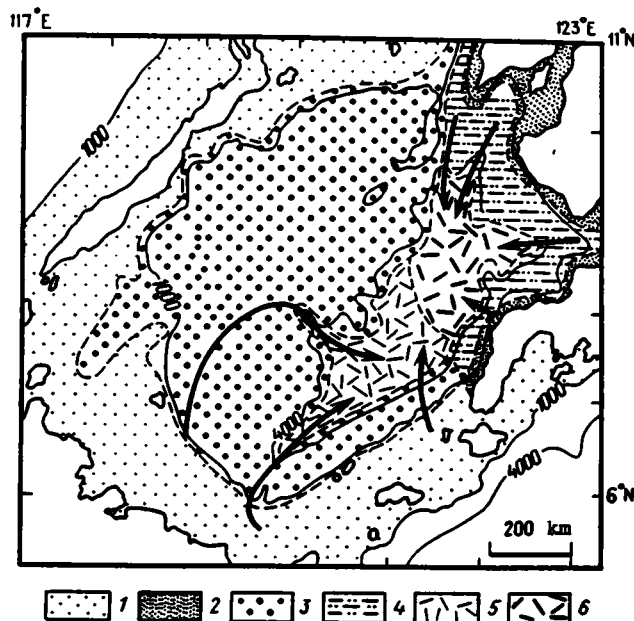


Fig. 1. Scheme of the distribution of basic sediment types and the postulated circulation paths of turbidite flows in the Sulu sea [10]: 1) limestone sands and gravels on solid bottom; 2) clay sands, gravels; 3) calcareous silts and muds; 4) argillaceous weakly sorted sediments (with silt); 5), 6) turbidites (5) calcareous varieties common; 6) calcareous varieties scarce). The direction of the turbidite flows is shown by arrows.

periods of time (beginning in the Eocene for the Banda arc), and it is connected with tectonic compression and thrust fault formation.

In addition to the mixtites, which are certainly of creep origin, there are formations of similar appearance that are widely distributed in the same structural position, but that are strongly tectonized, thicker, and sometimes also more polymict. Their origins are often connected exclusively with tectonic processes and they are considered to be unique tectonic breccia-mélanges. Disagreements exist in connection with the genetic interpretation of mixtites. Some treat the deposits as either olistostromes [10] or mélange [11]. Apparently, in a series of cases melanges may represent tectonized olistostromes or complex tectonic mixtures including olistostromal material together with other rocks and sediments. Certainly both gravitational-creep and tectonic processes are important in the Indonesian region, and the blocky mixtites they created are distributed very widely, occurring both among young deposits and in the Paleogene and Cretaceous sections.

Deposits of creep and pastelike flows are not only present in trenches. Locally they form large shelves in the marine trough on the continental slope and at its slope foot. Such accumulations up to 4500 km² in area have been revealed by acoustic methods in the South China sea [8]. They are bounded on the leading part by the steep surface of the break, and displaced blocks of stratified deposits are noted in them. A few core drilling tests taken within the limits of one of the creep zones are composed of grey clay with lenses of sand and silt, as well as with scarps and banks of green-grey clay. The creep zone horizons are sometimes coated by a cover of stratified sediments, and they are sometimes Recent formations.

Small creep shelves, several square kilometers in area, are detected here and there at the slope bases of underwater mountains in the sea. They preferably should be classified as not only olistostromes, but as avalanche accumulations (underwater colluvium).

The second type of mixtites is connected with mud volcano activity and clay diapirism. Clay diapirs are well established by seismoacoustic methods; on the surface they are crowned by mud volcanoes. They are mainly developed on the inner slopes of trenches and outer island

arc uplifts, where tectono-sedimentational "sections" (accretionary prisms) achieve great thickness. Diapirs may break through flat-lying stratified sequences of several kilometers, and their "apophyses" are injected between layered structures and surfaces of thrust faults [5]. Mud volcanoes and diapirs are often linear, tracing zones of shears.

Recent active volcanoes are found on several islands of the frontal Banda arc [5, 11]. The products of their activity ("breccia") form groups of hills (4-5 m high, sometimes containing ridges 200-300 m high and $(1-2.5) \times (5-18)$ km in size [6]. Depressions ("pot-holes") are observed on the surfaces and slopes of the hills. The floors are covered by grey clay, sometimes with oil spots and gurgling gas bubbles (methane?). The volcano deposits, as with the diapir bodies, are composed of nonhomogeneous "detached" and scaly clays sometimes of various shades (matrix) with included irregular block forms (somewhat similar to boudins) that are not in contact and that range from 1 cm to a few meters in size. The fragments vary in composition from place to place. Turbidite sandstones, cross-bedded volcaniclastics, black shales, red terrigenous clays and marls, reefogenic limestones generally occur among them; the rock ages (like the compositions) correspond to the stratigraphic units cut by the diapirs, while such units are multiply repeated in the section (thrust fault complexes). On the island of Timor, the detrital material of mixtites represents Permian, Triassic, Pliocene-Pleistocene rocks and Holocene reef limestones. Exotic fragments (serpentinites, metamorphites) occur in addition to the local fragments; it is assumed that they derive from lower horizons (layers) not revealed in outcrops or by faulting.

The phenomena of diapirism and mud volcanism are evidently connected with ellisional processes. However in this case they are occurring not in the typical ellisional sedimentary-rock basin with rapid sediment accumulation [2], but in zones where the basic mass is created by a thick thrust fault complex and where tectonic (compression) and seismic phenomena are widely apparent. As always, the process begins with dehydration and mineral transformation of clays,* leading to the segregation of a great quantity of water; this increases pore pressure. The presence of a gas-liquid phase of hydrocarbon intensifies it. The generated pressure gradient assists in the displacement of clay material. The processes develop most strongly in fault zones, where the permeability increases sharply. Observations on Timor showed that in shear zones the diapirs are "enriched" by local tectonic clastics.

Diapirs and mud volcanoes supply sedimentary material to the sedimentation zone, sometimes in great quantities. As a result of erosion and abrasion on islands it is "washed" of clay, while the remnant coarse fraction is rewashed and creates boulder-gravel accumulations (alluvial, beach); it is possible to find fragments of exotic rocks among them.

The second type of mixtites are outwardly similar to olistostromes, and therefore some authors relate the deposits to olistostromes [4], while others relate the same deposits [5] to mud volcanic breccias and diapirs. Since the latter well are documented and it is impossible to deny their presence, then their structure is explained by the primary olistostromal nature.

On the whole it is evident that both types of mixtites are widely distributed in Indonesia.

Flyschlike Sand-Clay Complexes. These are rhythmic interlayers of sands, silts, and clays or marls, representing the turbiditic hemipelagic facies complex†. Basic information on the deposits is obtained based on high frequency seismic profiling, which limits their lithological characteristics. However special investigations were conducted on the correlation of acoustic data and the composition of deposits, which also made it possible to confidently distinguish the upper part of the sedimentary cover of a series of facies complexes (seismo facies) including turbidites. In distinction from the seismic profiles cited above, on shelves the turbidite profiles are characterized by sharp and extended reflecting horizons. Supplementary information of sediments was obtained with the help of ground tubes.

Turbidite sequences in the considered region are developed in deep water trenches, sloped depressions, frontal troughs, and marginal seas.

*As in ellisional basins, the clay material experiences hydromicatization; on Timor, clays of diapirs and mud volcanoes are represented by mixed layer phases (illite 80%, smectite 20%), and pure smectite is absent.

†For brevity we will define such complexes as turbidites.

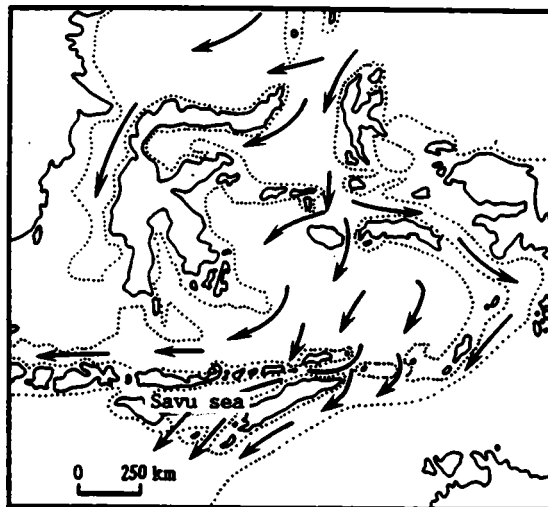


Fig. 2. Scheme of deep water (1000-1500 m) circulation in the eastern part of the Indonesian archipelago [17]. The dotted lines represent the 1000 m isobath.

In the trenches, turbidite sedimentation is principally carried out by longitudinal transport, although transverse currents also play a definite role. In large trenches the sources of supply and the quantity of clastics may vary along the structure, affecting the composition and thickness of sediments. The Java trench is a good example. A great volume of terrigenous material from the bay of Bengal is supplied to its northwest part, forming a "longitudinal turbidite wedge," the thickness of which decreases to the east. The width of the wedge in its proximal portion reaches approximately 30 km, while close to the eastern end of Sumatra it is less than 5 km. The thickness of the deposits decreases with distance from the supply source, and the hemipelagic component acquires greater value in their composition. The composition of clastics in the turbidites is polymict, but quartz, feldspars, and micas (sialic material) predominate. There is a lack of notable content of eroded products of the neighboring mountain structures (the islands of Sumatra and Java). This is connected with the depressions which form traps on the arc-trench transition.

Graded and layered textures (horizontal and dipping), convolution, uneven contacts and bases of coarser layers, and silty-pelitic "lumps" are noted in the deposits [3]. These are all signs characteristic of turbidites; individual turbidite units exceed 2.5 m. Interturbidite sedimentation is represented by grey-green silty pelites (hemi-pelagites).*

In addition to the longitudinal transportation of "alien" (Bengal) detrital material, a supplementary supply of clastics from the lower part of the inner trench slope has been established [13]. Small fans forming mildly sloping hills on the floor appear in it.

The thickness of the turbidite sequences varies. It is sometimes very great in the frontal troughs and depressions on the inner trench slopes. Longitudinal dispersion of material predominates in the trough-like depressions, as in trenches. In the central part of the structure, the sediments lie horizontally; they adjoin bounding uplifts or transform into creep accumulations at the slope foot.

In back and marginal troughs (Sula, Sulawesi, South China sea), the turbidite-hemipelagic complexes locally comprise a significant part of the sedimentary cover. They are represented by grey and green-grey clays alternating with sands, often fine and medium grained, although coarse grained varieties are also locally present; the latter are widely distributed in the Pleistocene. The average sand layer sequence reaches 5-10 cm, but both thinner (< 1 cm) and thicker (up to 3 cm) layers occur. Gradational structure is observed in the sandstones, and the deposits sometimes include every interval of the turbidity model.

*In several turbidite sequences bottom currents sediments are present, and it is necessary to define such complexes as turbidite-contourite-hemipelagic.

In the Sulu sea Holocene turbidite interlayers reach an approximate depth of 5 km (abyssal turbidites). Here, flyschlike rhythmicity is clearly expressed in the section. Fine grained sands or coarse silts are developed at the base of the rhythms, succeeded by laminated silty clay (silty pelite) which alternates with homogeneous clay (marly) silt. The sequence of rhythms averages 7 cm, while the limits of variation are from 2 cm to 1 m (the upper part of several rhythms is eroded).

Two types of rhythms are distinguished [10]: high carbonate and slightly carbonate. In the first type the lower part is primarily composed of bioclastic carbonate material, while shallow water forms of detritus predominates. The upper part represents a mixture of calcolithic and clay silt; coarser sediment comprises up to 60% of the section. In the second type of rhythm the deposits are less coarse; carbonate-terrigenous silty pelites, composing up to 20% of the section, lie in the lower portions of the rhythms, while weakly or noncarbonate clays lie in the upper. Such distinctions are caused by the differing character of the shelf from which the material entered. In the first case these were wide shelves richly populated by various marine invertebrates. In the second case they were narrow muddy shelves (see Fig. 1).

Large fields (25,000 km²) of migrating sediment waves ("underwater dunes") have been detected in the South China sea in a region of turbidite development; some investigators have connected them with turbid sedimentation, others with bottom currents (contourites). In any case, they are developed in places where a significant part of the deposits are turbidite formations.

Thus, the sequence of stratified terrigenous and carbonate-terrigenous deposits in the depressions of the complex systems of the Indonesian archipelago are represented by turbidites, contourites, and hemipelagic silts, which are arranged in space time conjunction (alternation in sections).

Clastics of diverse composition are characteristic for deposits overall. The composition is often polymict, including both mafic and sialic material, while the role of the latter is great and often predominating. This is also reflected in thin sediments, fine silts and clays, enriched by mica. The abundance of sialic clastics is determined not only by their input from the Asiatic continent, but also by the distinctive features of the inner supplying provinces (small continents, basement of large magmatic arcs).

Sequences exist where the main component is volcanitic clastics, sometimes with an admixture of shelly detritus (shallow water origin). Volcanic and volcano-bioclastic sands are predominantly found in island arcs, where folded basement is absent (or where it doesn't enter the erosion zone). Islands of the Sulu and Sangihe archipelagos may serve as an example [10, 15]. Here sands are formed in rather deep intrainland depressions. Thus, in the strait between two volcanic islands of Sangihe arc (at depths of ~1000 m) dark-olive and black volcanitic sands are developed with an admixture of foraminifera, shelly detritus and sponge spicules. A supplying canyon with a near mouth fan is detected on the slope of the depression, which makes it possible to relate the sands to turbidites [15]. Evidently sediment carried out by turbidite flow from the island shelf was redeposited in the strait by the bottom current.

The thickness of the stratified sequences, including turbidites, varies greatly: from tens of meters to 2-4 km. The average sedimentation rate for pelagic sediments in the Sulu sea is estimated at 9-16 cm/1000 years [10].

Layered Sand-Silty-Clay Complexes. These deposits along the sediment bank are close to those considered above, but they have distinct structural-textural characteristics. Bottom currents have the primary value in their formation. They are generally connected with bathyal depths, and both "normal" and redeposited hemipelagic silts take part in the structure of the complexes. We will define such complexes as contour-hemipelagic. They are probably widely distributed in the Indonesian region, but they have been given less consideration than turbidites. Detailed study of Quaternary deposits from the southern part of the Savu sea (Fig. 2) has exceptional value in understanding the formation conditions of the contourites.

The sea is located between Flores island, the Savu-Timor ridge, and Sumba island. It is composed of two troughs divided by a sublatitudinal underwater uplift (depth ~1000 m), which serves as a barrier, impeding the wide penetration of deep Pacific ocean waters into the Indian ocean. Foraminiferal sands are developed on the uplift. They are almost completely washed of their fine fraction, and have a CaCO₃ content reaching 83%. There are locally

TABLE 1. Major Facies Complexes of Marine Deposits in the Indonesian Archipelago (late Cenozoic-Holocene)

Zone	Deposits (rock associations)	Facies complexes and their formation mechanisms	Basic topography
Shallow water environment	Clay-silts, weakly carbonate, with lenses, interlayers, and packets of sand	Terrigenous shallow water with deltaic, littoral and neritic facies; separation of river material by waves and currents; settling of suspended material	Near continental shelves
	Limestones, shelly, detrital, skeletal sands; possible admixture of terrigenous material	Biogenic (benthic) limestone with littoral and neritic facies; the sedimentary component is skeletal remnants, partially reworked by wave hydrodynamics and currents	Near islands, seldom near continental shelves
	Limestones, organogenic, primary-framework and fragmental	Reef with facies: coral-algal structures, breccias (reef talus), calc-arenite shoals and lagoons	Volcanic and structural uplifts, shelf edges, remnant minicontinents
	Lumpy-silty pelitic mixtites with packets of sandstones and gravelites	Underwater gravitational and tectonogravitational slumps (olistostromes) and pastelike flows (debrites) with subordinate proximal turbidites	Inner slopes of trenches; seldom slopes of marine troughs
Zone of contrasting relief	Lumpy clay mixtites	Mud volcanoes, and clay diapirs; tectonoelisional processes	Island arc systems (accretionary complexes)
	Rhythmic alternation of sandstones, siltstones, pelites (clays, marls, limestones)	Turbidite-hemipelagic (varieties: terrigenous, volcanoterrigenous, limestone); facies are proximal, distal; gravitational flows of material; settling of suspended material from surface layers of basin	Trenches, troughs, (frontal arc, marginal seas)
Deep water environment	Sand-silt-pelitic (clay, marl, limestone)	Contourite-hemipelagic; bottom currents	Trenches, troughs, interisland straits
	Clay-calcareous muds (marls), green and grey	Hemipelagic terrigenous-biogenic (planktonogenic); may be ash; settling from suspension	Slopes and depressed marine zones
	Fine foraminiferal-coccolithic muds (limestones), green-grey, white	pelagic biogenic (planktonogenic); settling from suspension	Central parts of seas

many pteropod and gastropod fragments, and volcaniclastics are present. Seismic profiling has established fields of migrating (?) sediment waves. Southwest currents "plowed out" a "channel" in the uplift, thereby eroding up to 1 km of sediments. Erosional products entered the southern trough, forming here a thick (700-1000 m) stratified contourite sequence [17] composed of olive and olive-grey clays and clay-foraminiferal sediments with scarce interlayers of well sorted quartzo-feldspathic silts. The interlayers have the sharp bases and tops that are characteristic of contourites. The structural-tectonic features of the sediments, the traces of deep water erosion within the ridge limits, and the redeposition of material in trough indicate the great role of bottom currents in formation of the complex.* The area of its development is estimated at roughly 4000 km².

*Such currents are distinct from the contour currents of the open ocean, and the term "contourite" is conditionally applied.

The cited example has a significant value for understanding several features of the sedimentation in the Indonesian region in general. The complex system of communicating depressions among the mosaic of uplifts is favorable for the formation of both surface and deep currents. It is established that the water mass of the intermediate layer (depth 1000-1200 m) is transported from the western part of the Pacific ocean into the Indian ocean (see Fig. 2). The currents acquire great velocity in the relatively narrow "channels" and assist in the erosion and transport of a significant volume of sediments. Locally such currents completely eliminate the sedimentary cover, revealing the basaltic basement. This is observed for example, at depth of 1000 m between two volcanic uplifts of the Sangihe ridge [15].

Solid ground with sparse intermittent cover of friable sediments is detected in the system of bays of Balabak (between the islands of Kalimantan and Palawan). Sediments here are represented either by olive-grey calcareous silts, or coarse sands with foraminifera and shelly detritus. Ripple marks are locally detected.

Terrigenous-Biogenic Hemipelagic Deposits. Planktonogenic sediments with an admixture of fine terrigenous material (clay, silt) are commonly related to hemipelagic deposits; the quantity of the latter is significant, but < 50%. A green-grey color is characteristic of hemipelagites, indicative of the reducing conditions of diagenesis. P. Kuenen [16] wrote that roughly speaking hemipelagic silts are equivalent to bathyal sediments; this is not completely accurate, but here it is correct to stress their distinction from oxidized abyssal muds. Hemipelagic sediments are a significant part of many turbidite complexes, but they also form independent accumulations, covering wide areas in deep parts of marine troughs, on their slopes, and sometimes in trenches. The sediment composition and structure varies both in section and in area, although the overall character is preserved. The main distinctions between various representatives of hemipelagites are variations in calcium content and granulometry (silt content), and in this respect they occupy an intermediate position between pelagic and terrigenous deposits.

Study of surface sediments in the Sulu sea along a profile from the Palawan shelf to the abyssal plain showed [10] that below 500 m the primary granulometric fraction is silt (on average 63-66%), largely formed of biogenic material; pelite composes < 35%. The CaCO_3 content in the depth interval between 760 and 2362 m is rather constant (64.5 and 52.2%, respectively). The character of the adjacent shelf influences the sediment composition. In that sea, but in line with a narrow "low carbonate" shelf at depths of 200-1000 m, the CaCO_3 content is 13-23%, and strictly speaking, these are already not hemipelagic but terrigenous muds. However they comprise a single cover with the hemipelagites, and evidently they may be related to a single group.

In relatively small seas, such as the Sulu and Sulawesi seas, communication with the open ocean is limited by shallow (200-400 m) straits, and the near bottom waters of the troughs are depleted in oxygen (for the Sulawesi sea the oxygen content of oxygen reaches 1.7-2.3 cm^3/ℓ [16]. The content of C_{org} in the surface sediments (Sulu sea) has the following values: on the shelf it is < 0.2%, at depths up to 760 m it is 1.82-2.35%, further it gradually decreases, reaching 0.5% at a depth of 2400 m, and then at depths of 4800-4900 m it increases to 0.84%, apparently explained by a local decrease in the sedimentation rate. On the whole the C_{org} content in the sediments is higher than in the oceans, but lower than in upwelling zones [10]. The sediment color, with the exception of the upper oxidized film, is determined by the degree of reduction of the muds, and varies from dark grey to grey and green-grey. Bioturbation is widely developed, and it is particularly abundant at depths of 3000 m, where it has almost entirely wiped out layering; it is less intense on the depth interval 3000-4800 m, and it practically disappears deeper, where the sediments have a layered texture.

Biogenic (Planktonogenic) Calcareous Pelagic Deposits. Three types of sediments are known to be related to pelagic formations (pelagites): calcareous, siliceous muds, and "red abyssal clays." The two latter types are not noticeably distributed in Indonesia, while the calcareous muds are closely connected with hemipelagic muds, comprising a single sequence. Their basic components are nanofossils, forming from 35 to 60% of the sediment; a significant admixture is shells of planktonic foraminifera variously preserved (dependent on the position of the sediment in relation to the foraminiferal lysocline) and radiolaria (from 5 to 20%); a clay admixture reaches from 10 to 20%. Foraminiferal sometimes comprise independent interlayers, with almost all pelite washed out, representing foraminiferal contourites. Terrigenous silt, volcanoclastics, spicules of sponges, remnants of diatoms and algal detritus occur in insignificant quantity [20]. The sediment color is grey-olive of various shades; pyrite is present.

Pelagic sediments comprise the Quaternary section in the Timor trough (well 262) and together with hemipelagics are present in the deep part of the marine trough.

Basic data on the main facies complexes of marine deposits in the Indonesian geosynclinal region is presented in the Table 1.

The main sediment forming materials here are terrigenous-detrital and clay. The first represents both mafic and sialic clastics, while the latter is widely distributed and often predominates. This is determined by the fact that its sources were not only the continent and small continents, but also large island arcs with metamorphic rocks and granitoids predominating in their basements.

Volcano-terrigenous clastics also play a large role; in defined structural zones (for example, in frontal troughs) they predominate or even completely comprise the detrital fraction. Moreover, there is a noteworthy absence (or insignificant development) among the marine sections of thick truly volcanoclastic accumulations (tuffs), which are a significant part of many geosynclinal formations in continental fold belts and which are present in the island arc systems of the northwest periphery of the Pacific ocean. Tephroic accumulations in Indonesia are primarily concentrated in the terrigenous complexes. This is evidently determined by the specific type of island arcs connected with large areas of dry land (the islands of Sumatra and Java) and which represent the varieties of marginal-continental volcanic belts. The fine (ash) volcanoclastic portion was input into the atmosphere by explosions and dispersed among marine sediments, and some quantity (but generally a sharply subordinate one) is present in almost every type of deposits.

A significant component of the sediments is biogenic calcareous material. The location of the region in the tropic zone and the complex underwater relief was expressed in the composition of the bios. In addition to planktonic forms, various benthonic invertebrate calcareous algae, including reef building forms have a large value here. Although the calcareous sediments are exceeded by terrigenous sediments in the volumetric relations, they impart a special appearance to the sedimentary formations on the whole.

In addition, there is a conspicuous absence of any notable accumulations of silicon (there are not siliceous complexes). None have been found, and if they have developed, then they must be insignificant, eupelagic "red beds." The primary mass of fine deep water muds is related to the category of reduced muds.

From the viewpoint of a sedimentation mechanism, gravity flows have a large value, including not only turbidites (s. lato), but also coarse chaotic accumulations of pastelike flows and slumps (tectonogravitational and gravitational olistostromes). Mélanges are spatially associated with them, and although mélanges are not related to sedimentation but to tectonic formation, their similar associations are not random, and are determined by features of the region's tectonic development.

It is possible to link the topographic-bathymetric environments (where material of varied origin is deposited by one of another method) to three main categories: shallow water regions, tectonically unstable zones of contrasting relief, and deep water basins.

Epicontinental seas (for example, Malay and Java), wide shelves (east Andaman, Palawan), and inner basin uplifts (Spratly) belong to the first category. Depending on the source of sedimentary material, only weakly carbonate terrigenous deposits, generally clay-silt, or limestones (organic-detrital and biohermic) are formed in the shallow water conditions (see Table 1).

Primarily arc-trench transitions are related to the second category. These include frontal troughs, and the outer arc and trench. This is the "kingdom" of various gravity flows: turbidites, debrites and olistostromes; mud volcanoes are also concentrated here. Deposits with similar formation mechanisms (turbidites, slump accumulations) also arise on the slopes of back trough seas (see table), particularly where such slopes are deposited by tectonic ledges (terraces).

Finally, the third category encompasses the deep water part of the archipelago: marine troughs and trenches. Hemipelagic and pelagic muds predominate here (sediments of biogenic and fine terrigenous suspended material); such peaceful "background" sedimentation is locally complicated by bottom currents, while the fine sands and silts of distal turbidites reach this region with time (see table).

Each of the facies complexes represents a regular association of sediments, of varied formation mechanisms. Strictly speaking these are paragenetic associations of defined genetic types of deposits. Complexes with similar formation mechanisms are distinguished in different cases by the origin of the sediment forming material; we have seen that the detrital material of the turbidites may be terrigenous sialic, volcanic, organogenic, and combinations of these materials; apparently, it is necessary to relate deposits with differing composition but similar formation conditions to variations of a single type of complex.

In a majority of cases the above cited complexes are connected with gradual transitions in sedimentational-genetic relations, and as was shown by analysis of actual material, they do not always yield precise delineation. However they form regular series, which is also reflected in their lateral intertransitions.

If one includes the marginal continental territories, which are not related to the geosynclinal region, but are deeply incorporated in it (Java sea), and which play a large role in the supply of sedimentary material to the geosyncline, then shallow water deposits have a second degree value even in the Indonesian archipelago (although it is probably greater here than in the majority of other systems). The deposits of the volcanic arcs are primary in "expression" and volume (s. lato). These are not simply zones of contrasting relief and gravity accumulations, but also of intensive collisional tectonics, accompanied also by obductive and subductive processes. These may all be connected with the defined (relatively late) stage of developments of the geosyncline, but they may also depend on the regional geodynamic features: collisions not of oceanic and continental plates, but collisions of two continents (the Asiatic with an active margin and the Australian with a passive margin).

A characteristic of the Indonesian region is the rather large number of depressed oceanic crustal basins with relatively small sizes. This has led to their somewhat isolated state, which is expressed in the appearance of the sediments.

It is probable that there have been geosynclinal regions in the past that are close to the Indonesian example, and certainly geosynclines with mosaic structure are related to them. It is necessary to assume that we do not encounter among them precise analogs of the facies complexes considered above (particularly when relating to the Paleozoic), since the evolution of the biosphere, and possibly the hydrosphere, is expressed in the sedimentation; in every case this is related to pelagic facies. However it is possible to hope that the overall character of deposits and their distribution will be similar.

LITERATURE CITED

1. I. V. Khvorova, "Sedimentation features in the Indonesian geosynclinal region, Report 1," *Litol. Polezn. Iskop.*, No. 3, 100-111 (1989).
2. V. N. Kholodov, *Post-Sedimentational Transformation in Ellisional Basins* [in Russian], Nauka, Moscow (1983).
3. W. A. Anikouchine and H. Y. Ling, "Evidence for turbidite accumulation in trenches in the Indo-Pacific region," *Marine Geol.*, 5, No. 2, 141-154 (1967).
4. M. G. Audley-Charles, "A Miocene gravity slide deposit from eastern Timor," *Geol. Mag.*, 102, No. 2, 267-276 (1965).
5. A. J. Barber, S. Tjokrosapoetro, and T. R. Charlton, "Mud volcanoes, wrench faults, and mélanges in accretionary complexes, eastern Indonesia," *Bull. Am. Assoc. Petrol. Geol.*, 70, No. 11, 2038-2043 (1986).
6. N. Breen, E. A. Silver, and D. M. Hussong, "Structural styles of an accretionary wedge south of the island of Sumba, Indonesia, revealed by MARC II side scan sonar," *Bull. Geol. Soc. Am.*, 97, No. 10, 1250-1261 (1986).
7. P. Y. Chen, "Minerals in bottom sediments of the South China sea," *Bull. Geol. Soc. Am.*, 89, No. 2, 212-222 (1978).
8. J. E. Damuth, "Quaternary sedimentation processes in the South China basin as revealed by echo-character mapping and piston-core studies," in: *The Tectonic and Geologic Evolution of Southeast Asian Seas and Islands*, (1980), pp. 105-126.
9. K. O. Emery and H. Nino, "Sediments of the Gulf of Thailand and the adjacent continental shelf," *Bull. Geol. Soc. Am.*, 74, No. 5, 541-554 (1963).
10. N. F. Exon, F. W. Haake, M. Hartman, et al., "Morphology, water characteristics, and sedimentation in the silled Sulu sea, Southeast Asia," *Marine Geol.*, No. 3/4, 165-195 (1981).
11. W. Hamilton, *Tectonics of the Indonesian Region*, U. S. Geol. Surv. Prof. Paper, No. 1078 (1979).

12. D. E. Karig, G. E. Moore, J. R. Curray, et al., "Morphology and shallow structure of the lower trench slope of Nias island, Sunda arc," in: *The Tectonic and Geologic Evolution of Southeast Asian Seas and Islands*, (1980), pp. 179-208.
13. J. A. Katili, "Volcanism and plate tectonics in Indonesian island arcs," *Tectonophysics*, 26, No. 3/4 165-188 (1975).
14. G. H. Keller and A. F. Richards, "Sediments in the Malacca strait, Southeast Asia," *J. Sediment. Petrol.*, 37, No. 1, 102-127 (1967).
15. D. C. Krause, "Tectonic marine geology and bathymetry of the Celebes sea-Sulu sea region," *Bull. Geol. Soc. Am.*, 77, No. 8, 813-832 (1966).
16. P. H. Kuenen, *Marine Geology*, Wiley, New York (1950).
17. D. L. Reed, A. W. Meyer, E. A. Silver, and H. Prasetyo, "Conturite sedimentation in an intraoceanic forearc system: eastern Sunda arc, Indonesia," *Marine Geol.*, 76, No. 3/4, 223-241 (1987).
18. H. H. Roberts, C. V. Phipps, and L. Effendi, "Halimeda bioherms of the eastern Java sea, Indonesia," *Geology*, 15, No. 4, 371-374 (1987).
19. K. S. Rodolfo, "Sediments of the Andaman basin, northeastern Indian ocean," *Marine Geol.*, 7, No. 5, 371-402 (1969).
20. J. J. Veevers, J. R. Heitzler, H. M. Bolli, et al., *Initial Reports of DSDP*, Vol. 27, Washington (1974).

DIFFERENCES BETWEEN BIRNESSITES OF SEDIMENTARY AND HYDROTHERMAL ORIGIN

L. E. Shterenberg, V. A. Drits,
A. L. Salyn', and N. L. Kalashnikova

UDC 553.32:552.313

The behavior of marine birnessites of different origins during heating has been examined. It has been determined that sedimentary birnessites convert to spinel at lower temperatures than the hydrothermal varieties. This can be used as an additional criterion in determining the genesis of marine Fe-Mn crusts and nodules.

Statement of the Problem. The source of the metal during the formation of nodules and cores is a matter of dispute.

Nodules and cores are known to be formed by both sedimentary and hydrothermal processes, with specific geological conditions determining which plays the major role.

Several workers [9 and 18, among others] have attempted to identify characteristics, that would make it possible to determine the origin of marine Fe-Mn formations.

It has been found that hydrothermal Fe-Mn nodules and crusts, unlike their sedimentary analogs, have the following characteristics: a clear-cut separation of the manganese and iron minerals, i.e., they go into segregated phases; low concentrations of such trace elements as Ni, Cu, and Co; a rapid rate of formation; elevated uranium:thorium ratios, and the like (Table 1).

The mineralogical characteristics of Fe-Mn nodules and crusts of different origins are not always clearly differentiated. For example, birnessites are encountered in both sedimentary and hydrothermal ore formations. At the same time, one naturally assumes that there must be some subtle structural or crystal-chemical differences between minerals of the same type formed under different conditions.

The purpose of the work reported here was to demonstrate the validity of this assumption by studying birnessites of hydrothermal and sedimentary origins.

Samples and Method of Study. The samples selected for study were birnessites, which were compared for genetic markers as well as for features determined by electron diffraction,

Geological Institute, Academy of Sciences of the USSR, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 4, pp. 17-29, July-August, 1989. Original article submitted August 12, 1988.

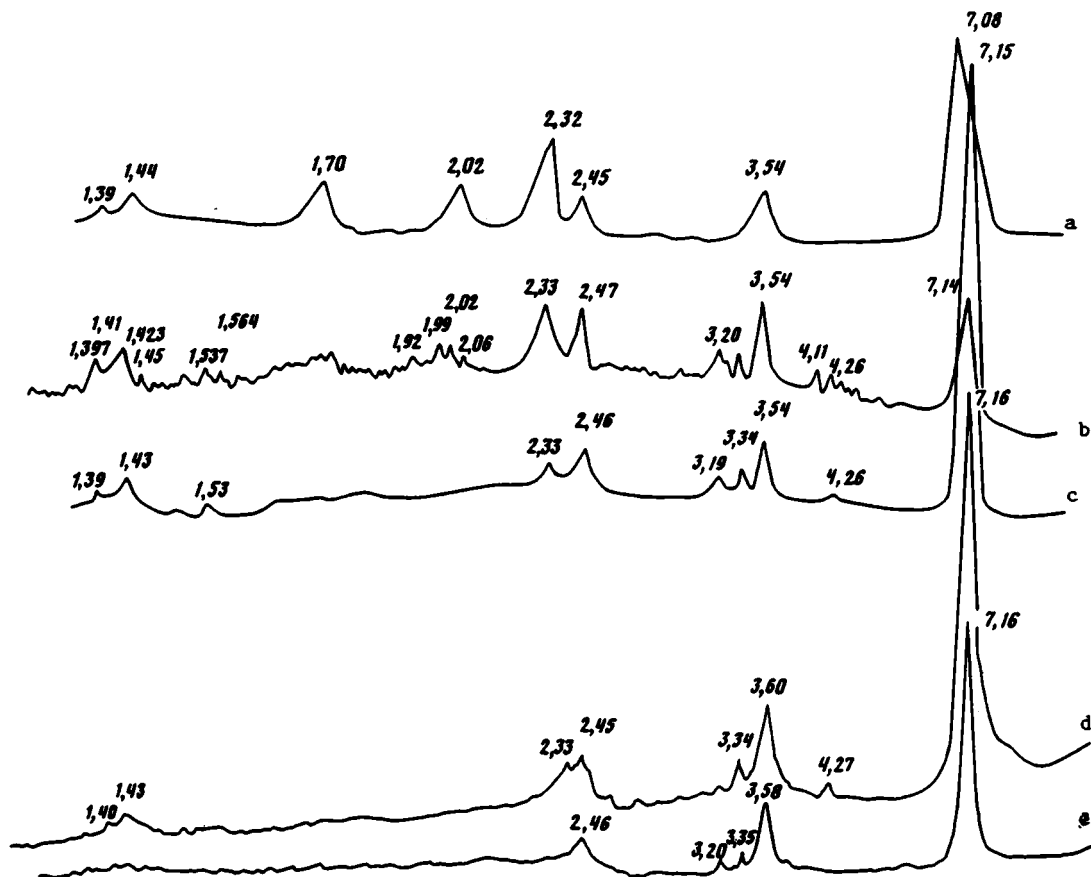


Fig. 1. Diffractograms of the birnessites studied. a) Fe-Mn micronodules (Pacific Ocean [5]); b) Type II Fe-Mn micronodules (Site 645, Voyage 9 of the RV Dmitrii Mendeleev); c) the same (Site 649); d) bottom of a manganese crust (Japan Sea, Station 2069); e) manganese lens from tephroidal sandstone (Sea of Okhotsk, Simushir island, Station 2716).

x-ray diffraction, and chemical analysis. Attention was focussed on the features the two types of birnessite exhibited in phase transitions at different temperatures.

There were several reasons for selecting birnessite. This manganese mineral is widely distributed throughout the oceans, and as noted above, is found in sedimentary and hydrothermal formations. It is more stable with respect to many transitions than other manganese minerals such as asbolite-buserite, buserite I, and buserite II [1]. According to data published in [12], birnessite should have the same structure as chalcophanite ($\text{Zn}_3\text{Mn}_6\text{O}_{14} \cdot 3\text{H}_2\text{O}$). F. V. Chukhrov and his coworkers at the Geological Institute and the IGEM [Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry] of the USSR Academy of Sciences [3, 5] utilized a number of methods (electron diffraction, depth profiling using x-ray powder diffraction patterns, microprobe analysis, and x-ray photoelectron spectroscopy) in a more detailed study of the birnessite structure. They studied micronodules collected during the 28th voyage of the research vessel [RV] Dmitrii Mendeleev at the Clarion-Clipperton nodule province [1].

According to the data published in [3, 4, 5], the birnessite structure is made up of octahedral Mn^{4+} layers (with Mg replacing some of the Mn) with a statistical distribution of defect (empty) octahedra with interlayer Mn^{3+} , Ca, K, and Na cations above and below the planes. Neighboring Mn^{4+} planes have the same azimuthal orientation and overlie each other in such a way that the projections of their octahedral cations coincide on the base plane. The empty octahedra in the mixed layers are distributed randomly, and do not fall on the same axis. Water molecules and the hydroxyls between the layers with oxygen atoms form one of the two mixed Mn^{4+} layers of octahedra occupied by the interlayer cations, and with the oxygen atoms of the other they form empty prisms. The structure of the birnessite studied has about 10 percent packing defects.

Pelagic sediments comprise the Quaternary section in the Timor trough (well 262) and together with hemipelagics are present in the deep part of the marine trough.

Basic data on the main facies complexes of marine deposits in the Indonesian geosynclinal region is presented in the Table 1.

The main sediment forming materials here are terrigenous-detrital and clay. The first represents both mafic and sialic clastics, while the latter is widely distributed and often predominates. This is determined by the fact that its sources were not only the continent and small continents, but also large island arcs with metamorphic rocks and granitoids predominating in their basements.

Volcano-terrigenous clastics also play a large role; in defined structural zones (for example, in frontal troughs) they predominate or even completely comprise the detrital fraction. Moreover, there is a noteworthy absence (or insignificant development) among the marine sections of thick truly volcanoclastic accumulations (tuffs), which are a significant part of many geosynclinal formations in continental fold belts and which are present in the island arc systems of the northwest periphery of the Pacific ocean. Tephroic accumulations in Indonesia are primarily concentrated in the terrigenous complexes. This is evidently determined by the specific type of island arcs connected with large areas of dry land (the islands of Sumatra and Java) and which represent the varieties of marginal-continental volcanic belts. The fine (ash) volcanoclastic portion was input into the atmosphere by explosions and dispersed among marine sediments, and some quantity (but generally a sharply subordinate one) is present in almost every type of deposits.

A significant component of the sediments is biogenic calcareous material. The location of the region in the tropic zone and the complex underwater relief was expressed in the composition of the bios. In addition to planktonic forms, various benthonic invertebrate calcareous algae, including reef building forms have a large value here. Although the calcareous sediments are exceeded by terrigenous sediments in the volumetric relations, they impart a special appearance to the sedimentary formations on the whole.

In addition, there is a conspicuous absence of any notable accumulations of silicon (there are not siliceous complexes). None have been found, and if they have developed, then they must be insignificant, eupelagic "red beds." The primary mass of fine deep water muds is related to the category of reduced muds.

From the viewpoint of a sedimentation mechanism, gravity flows have a large value, including not only turbidites (s. lato), but also coarse chaotic accumulations of pastelike flows and slumps (tectonogravitational and gravitational olistostromes). Mélanges are spatially associated with them, and although mélanges are not related to sedimentation but to tectonic formation, their similar associations are not random, and are determined by features of the region's tectonic development.

It is possible to link the topographic-bathymetric environments (where material of varied origin is deposited by one of another method) to three main categories: shallow water regions, tectonically unstable zones of contrasting relief, and deep water basins.

Epicontinental seas (for example, Malay and Java), wide shelves (east Andaman, Palawan), and inner basin uplifts (Spratly) belong to the first category. Depending on the source of sedimentary material, only weakly carbonate terrigenous deposits, generally clay-silt, or limestones (organic-detrital and biohermic) are formed in the shallow water conditions (see Table 1).

Primarily arc-trench transitions are related to the second category. These include frontal troughs, and the outer arc and trench. This is the "kingdom" of various gravity flows: turbidites, debrites and olistostromes; mud volcanoes are also concentrated here. Deposits with similar formation mechanisms (turbidites, slump acculations) also arise on the slopes of back trough seas (see table), particularly where such slopes are deposited by tectonic ledges (terraces).

Finally, the third category encompasses the deep water part of the archipelago: marine troughs and trenches. Hemipelagic and pelagic muds predominate here (sediments of biogenic and fine terrigenous suspended material); such peaceful "background" sedimentation is locally complicated by bottom currents, while the fine sands and silts of distal turbidites reach this region with time (see table).

Each of the facies complexes represents a regular association of sediments, of varied formation mechanisms. Strictly speaking these are paragenetic associations of defined genetic types of deposits. Complexes with similar formation mechanisms are distinguished in different cases by the origin of the sediment forming material; we have seen that the detrital material of the turbidites may be terrigenous sialic, volcanic, organogenic, and combinations of these materials; apparently, it is necessary to relate deposits with differing composition but similar formation conditions to variations of a single type of complex.

In a majority of cases the above cited complexes are connected with gradual transitions in sedimentational-genetic relations, and as was shown by analysis of actual material, they do not always yield precise delineation. However they form regular series, which is also reflected in their lateral intertransitions.

If one includes the marginal continental territories, which are not related to the geosynclinal region, but are deeply incorporated in it (Java sea), and which play a large role in the supply of sedimentary material to the geosyncline, then shallow water deposits have a second degree value even in the Indonesian archipelago (although it is probably greater here than in the majority of other systems). The deposits of the volcanic arcs are primary in "expression" and volume (s. lato). These are not simply zones of contrasting relief and gravity accumulations, but also of intensive collisional tectonics, accompanied also by obductive and subductive processes. These may all be connected with the defined (relatively late) stage of developments of the geosyncline, but they may also depend on the regional geodynamic features: collisions not of oceanic and continental plates, but collisions of two continents (the Asiatic with an active margin and the Australian with a passive margin).

A characteristic of the Indonesian region is the rather large number of depressed oceanic crustal basins with relatively small sizes. This has led to their somewhat isolated state, which is expressed in the appearance of the sediments.

It is probable that there have been geosynclinal regions in the past that are close to the Indonesian example, and certainly geosynclines with mosaic structure are related to them. It is necessary to assume that we do not encounter among them precise analogs of the facies complexes considered above (particularly when relating to the Paleozoic), since the evolution of the biosphere, and possibly the hydrosphere, is expressed in the sedimentation; in every case this is related to pelagic facies. However it is possible to hope that the overall character of deposits and their distribution will be similar.

LITERATURE CITED

1. I. V. Khvorova, "Sedimentation features in the Indonesian geosynclinal region, Report 1," *Litol. Polezn. Iskop.*, No. 3, 100-111 (1989).
2. V. N. Kholodov, *Post-Sedimentational Transformation in Ellisional Basins* [in Russian], Nauka, Moscow (1983).
3. W. A. Anikouchine and H. Y. Ling, "Evidence for turbidite accumulation in trenches in the Indo-Pacific region," *Marine Geol.*, 5, No. 2, 141-154 (1967).
4. M. G. Audley-Charles, "A Miocene gravity slide deposit from eastern Timor," *Geol. Mag.*, 102, No. 2, 267-276 (1965).
5. A. J. Barber, S. Tjokrosapoetro, and T. R. Charlton, "Mud volcanoes, wrench faults, and mélanges in accretionary complexes, eastern Indonesia," *Bull. Am. Assoc. Petrol. Geol.*, 70, No. 11, 2038-2043 (1986).
6. N. Breen, E. A. Silver, and D. M. Hussong, "Structural styles of an accretionary wedge south of the island of Sumba, Indonesia, revealed by MARC II side scan sonar," *Bull. Geol. Soc. Am.*, 97, No. 10, 1250-1261 (1986).
7. P. Y. Chen, "Minerals in bottom sediments of the South China sea," *Bull. Geol. Soc. Am.*, 89, No. 2, 212-222 (1978).
8. J. E. Damuth, "Quaternary sedimentation processes in the South China basin as revealed by echo-character mapping and piston-core studies," in: *The Tectonic and Geologic Evolution of Southeast Asian Seas and Islands*, (1980), pp. 105-126.
9. K. O. Emery and H. Nino, "Sediments of the Gulf of Thailand and the adjacent continental shelf," *Bull. Geol. Soc. Am.*, 74, No. 5, 541-554 (1963).
10. N. F. Exon, F. W. Haake, M. Hartman, et al., "Morphology, water characteristics, and sedimentation in the silled Sulu sea, Southeast Asia," *Marine Geol.*, No. 3/4, 165-195 (1981).
11. W. Hamilton, *Tectonics of the Indonesian Region*, U. S. Geol. Surv. Prof. Paper, No. 1078 (1979).

12. D. E. Karig, G. E. Moore, J. R. Curray, et al., "Morphology and shallow structure of the lower trench slope of Nias island, Sunda arc," in: *The Tectonic and Geologic Evolution of Southeast Asian Seas and Islands*, (1980), pp. 179-208.
13. J. A. Katili, "Volcanism and plate tectonics in Indonesian island arcs," *Tectonophysics*, 26, No. 3/4 165-188 (1975).
14. G. H. Keller and A. F. Richards, "Sediments in the Malacca strait, Southeast Asia," *J. Sediment. Petrol.*, 37, No. 1, 102-127 (1967).
15. D. C. Krause, "Tectonic marine geology and bathymetry of the Celebes sea-Sulu sea region," *Bull. Geol. Soc. Am.*, 77, No. 8, 813-832 (1966).
16. P. H. Kuenen, *Marine Geology*, Wiley, New York (1950).
17. D. L. Reed, A. W. Meyer, E. A. Silver, and H. Prasetyo, "Conturite sedimentation in an intraoceanic forearc system: eastern Sunda arc, Indonesia," *Marine Geol.*, 76, No. 3/4, 223-241 (1987).
18. H. H. Roberts, C. V. Phipps, and L. Effendi, "Halimeda bioherms of the eastern Java sea, Indonesia," *Geology*, 15, No. 4, 371-374 (1987).
19. K. S. Rodolfo, "Sediments of the Andaman basin, northeastern Indian ocean," *Marine Geol.*, 7, No. 5, 371-402 (1969).
20. J. J. Veevers, J. R. Heitzler, H. M. Bolli, et al., *Initial Reports of DSDP*, Vol. 27, Washington (1974).

DIFFERENCES BETWEEN BIRNESSITES OF SEDIMENTARY AND HYDROTHERMAL ORIGIN

L. E. Shterenberg, V. A. Drits,
A. L. Salyn', and N. L. Kalashnikova

UDC 553.32:552.313

The behavior of marine birnessites of different origins during heating has been examined. It has been determined that sedimentary birnessites convert to spinel at lower temperatures than the hydrothermal varieties. This can be used as an additional criterion in determining the genesis of marine Fe-Mn crusts and nodules.

Statement of the Problem. The source of the metal during the formation of nodules and cores is a matter of dispute.

Nodules and cores are known to be formed by both sedimentary and hydrothermal processes, with specific geological conditions determining which plays the major role.

Several workers [9 and 18, among others] have attempted to identify characteristics, that would make it possible to determine the origin of marine Fe-Mn formations.

It has been found that hydrothermal Fe-Mn nodules and crusts, unlike their sedimentary analogs, have the following characteristics: a clear-cut separation of the manganese and iron minerals, i.e., they go into segregated phases; low concentrations of such trace elements as Ni, Cu, and Co; a rapid rate of formation; elevated uranium:thorium ratios, and the like (Table 1).

The mineralogical characteristics of Fe-Mn nodules and crusts of different origins are not always clearly differentiated. For example, birnessites are encountered in both sedimentary and hydrothermal ore formations. At the same time, one naturally assumes that there must be some subtle structural or crystal-chemical differences between minerals of the same type formed under different conditions.

The purpose of the work reported here was to demonstrate the validity of this assumption by studying birnessites of hydrothermal and sedimentary origins.

Samples and Method of Study. The samples selected for study were birnessites, which were compared for genetic markers as well as for features determined by electron diffraction,

Geological Institute, Academy of Sciences of the USSR, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 4, pp. 17-29, July-August, 1989. Original article submitted August 12, 1988.

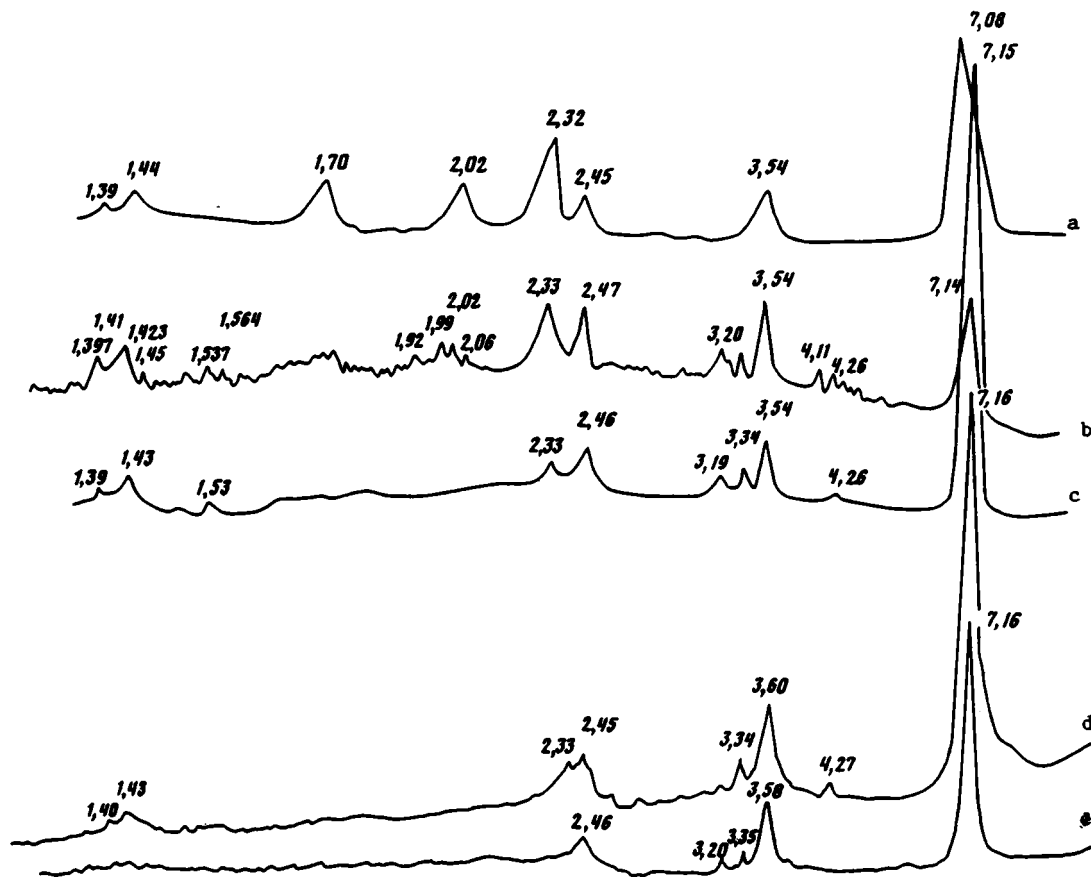


Fig. 1. Diffractograms of the birnessites studied. a) Fe-Mn micronodules (Pacific Ocean [5]); b) Type II Fe-Mn micronodules (Site 645, Voyage 9 of the RV Dmitrii Mendeleev); c) the same (Site 649); d) bottom of a manganese crust (Japan Sea, Station 2069); e) manganese lens from tephroidal sandstone (Sea of Okhotsk, Simushir island, Station 2716).

x-ray diffraction, and chemical analysis. Attention was focussed on the features the two types of birnessite exhibited in phase transitions at different temperatures.

There were several reasons for selecting birnessite. This manganese mineral is widely distributed throughout the oceans, and as noted above, is found in sedimentary and hydrothermal formations. It is more stable with respect to many transitions than other manganese minerals such as asbolite-buserite, buserite I, and buserite II [1]. According to data published in [12], birnessite should have the same structure as chalcophanite ($\text{Zn}_3\text{Mn}_6\text{O}_{14} \cdot 3\text{H}_2\text{O}$). F. V. Chukhrov and his coworkers at the Geological Institute and the IGEM [Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry] of the USSR Academy of Sciences [3, 5] utilized a number of methods (electron diffraction, depth profiling using x-ray powder diffraction patterns, microprobe analysis, and x-ray photoelectron spectroscopy) in a more detailed study of the birnessite structure. They studied micronodules collected during the 28th voyage of the research vessel [RV] Dmitrii Mendeleev at the Clarion-Clipperton nodule province [1].

According to the data published in [3, 4, 5], the birnessite structure is made up of octahedral Mn^{4+} layers (with Mg replacing some of the Mn) with a statistical distribution of defect (empty) octahedra with interlayer Mn^{3+} , Ca, K, and Na cations above and below the planes. Neighboring Mn^{4+} planes have the same azimuthal orientation and overlie each other in such a way that the projections of their octahedral cations coincide on the base plane. The empty octahedra in the mixed layers are distributed randomly, and do not fall on the same axis. Water molecules and the hydroxyls between the layers with oxygen atoms form one of the two mixed Mn^{4+} layers of octahedra occupied by the interlayer cations, and with the oxygen atoms of the other they form empty prisms. The structure of the birnessite studied has about 10 percent packing defects.

TABLE 1. Comparison of Hydrothermal (I) and Sedimentary (II) Fe-Mn Marine Formations [18]

Index	I		II		
	sediments	ore formation	sediments	crusts	nodules
Fe/Mn	< 0.1 and > 0.1	Fe-rich: 12-237 Mn-rich 0.002-0.14	0.5-5.0	≈ 1	≈ 1
Trace element content	Low	Low	High	High	High
U/Th	> 1	> 1	< 1	< 1	< 1
Accumulation	Rapid	100-1000 mm in 10 ⁶ yrs	Slow	1-10 mm in 10 ⁶ yrs	1-10 mm in 10 ⁶ yrs

We have studied the same sedimentary birnessite studied by V. A. Drits et al. [1] and F. V. Chukhrov et al. [3, 5].

This is the major ore mineral of the Type II Fe-Mn micronodules [7] collected from the Pacific Ocean bottom during Voyage 9 of the RV Dmitrii Mendeleev at Station 645 (18°33' north, 146°59' west, at 5350 m) and at Station 649 (17°58' north, 130°09' west, at 4950 m).

At Station 645, the Fe-Mn micronodules were collected from a depth of 230-240 cm from red pelagic oozes enriched in zeolites. The composition and structure of these micronodules, which we have classified as Type II nodules, have been studied previously [7]. These formations exhibit a wide range of shapes (rodlike, spherical) under the binocular microscope. They are dark gray and have a slight metallic luster and a smooth surface. They separate easily when pressed gently with a needle. In reflected light, microaggregations of ore formations of different reflectances are visible. Under crossed Nicols, the ore formations remain isotopic, evidence of the extremely small size of the particles comprising them. X-ray diffraction (cf. Fig. 1b) of the Station 645 micronodules showed that they consist largely of birnessite.

Similar Type II Fe-Mn micronodules were also collected at Station 649. They were found at a depth of 245-260 cm in red pelagic oozes containing siliceous microorganisms. Judging from the x-ray diffraction evidence, these micronodules also consist largely of birnessite (cf. Fig. 1c).

Electron diffraction data confirmed the x-ray diffraction evidence that the major mineral in the micronodules collected at Stations 645 and 649 is birnessite; it also identified very subordinate amounts of vernadite and hydrogoethite in them.

Localized x-ray energy-dispersive analysis showed that the birnessite particles do not contain iron.

The hydrothermal birnessite samples were collected from Fe-Mn formations in the Sea of Japan and the Sea of Okhotsk. Birnessite was discovered in the Sea of Japan during Voyage 36 of the RV Pervenets in the bottom of a 2-cm ore crust from Station 2069 (41°25' north, 134°59' east).

The ore formations studied are massive and very dense. They have columnar segregations seen to be coated by later manganese segregations when viewed in reflected light; these were identified by electron diffraction as vernadite. The nodule is steel-gray in color and has a typical metallic luster. X-ray diffraction (Fig. 1d) and electron diffraction [6] showed that the bottom of the crust taken for study is actually birnessite.

The hydrothermal birnessite discovered in the Sea of Okhotsk is in the form of thin lenses, inclusions, and interlayers among the unsorted tephoidal sandstones collected during Voyage 27 of the RV Pegas near the island of Simushir at Station 2716 (47°20'; 151°42'). It is dense and massive, gray in color, with a clearly visible columnar segregation and a metallic luster. In reflected light these samples too are seen to consist of micrograins. Analysis by a number of techniques confirmed that the major mineral comprising the ore lenses is birnessite [8].

TABLE 2. Major and Trace Elements in Birnessites of Different Origins, %

Sampling site	MnO	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	NiO	CoO	CuO	Birnessite type
Pacific Ocean, Station 645	30,3	8,5	3,5	2,3	0,7	0,3	1,30	0,21	0,95	Sedimentary
Pacific Ocean, Station 649	34,2	2,4	2,1	3,1	0,6	0,8	1,45	0,33	0,43	"
Caribbean [13]	60,6	1,2	0,4	6,2	1,9	1,8	0,80	0,14	0,33	"
Pacific Ocean [5]	57,2	N.d.	0,5	8,6	1,9	2,9	N.d.	N.d.	N.d.	"
Pacific Ocean [7]	30,6	6,8	N.d.	N.d.	N.d.	N.d.	1,63	0,16	0,92	"
Sea of Japan [6]	77,5	0,5	2,3	2,6	6,0	1,4	0,08	0,04	0,06	Hydrothermal
Sea of Okhotsk [8]	89,1	0,13	3,4	1,2	5,6	0,4	0,04	0,001	0,007	"
Pacific Ocean [10]*	62,2	0,7	2,3	1,9	8,6	1,5	0,012	0,002	0,011	"
Pacific Ocean [16]**	77,9	0,2	2,3	4,4	1,9	1,7	0,21	0,12	0,25	"

*Average of five analyses.

**Average of three analyses.

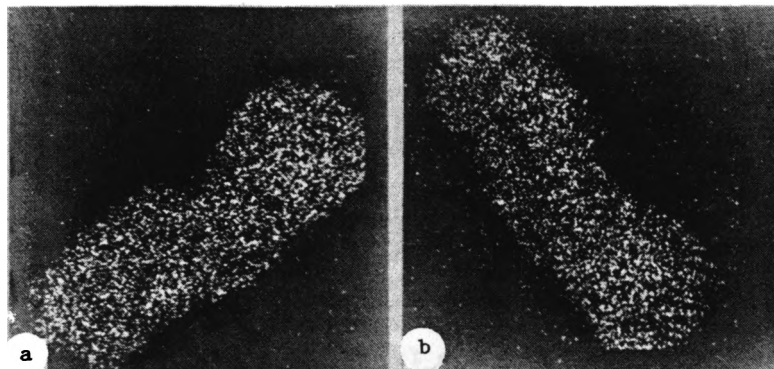


Fig. 2. Type II Fe-Mn micronodules (birnessite composition), Station 649 (Pacific Ocean) in x-ray characteristic radiation, magnification 280× (a - MnK α ; b - FeK α).

The x-ray diffraction patterns of the sedimentary and hydrothermal birnessites from the Pacific Ocean, the Sea of Japan, and the Sea of Okhotsk allow one to evaluate how similar their structures are (cf. Fig. 1). Other evidence of this is provided by the x-ray analyses made by a number of workers studying birnessites of different origins.

Table 2 presents the results of chemical analyses of birnessites of sedimentary and hydrothermal origins evidencing the existence of certain differences between them. The hydrothermal birnessites generally have significantly (an order of magnitude) higher Mn/Fe ratios and lower (by one or two orders of magnitude) concentrations of such trace elements as nickel, copper, and cobalt.

These differences are obviously due to characteristic features of the formation of marine Fe-Mn macro- and micronodules of different origins that result in different accumulations of the elements referred to (cf. Table 1).

At the same time, one cannot rule out the possibility that different manganese and iron contents in sedimentary and hydrothermal birnessites are due to different degrees of cleanliness observed in collecting the samples for analysis. In particular, manganese and iron minerals in sedimentary formations are so closely related genetically (cf. Fig. 2) that it is virtually impossible to distinguish them even with the aid of an electron x-ray microanalyzer.

Experimental. D. G. Golden et al. [14] studied thermal transitions of synthetic birnessites saturated with various exchange cations. They found that different mineral phases form when birnessites are heated for 2 h at 200°, 400°, 600°, and 800°C. The course of the transition as the birnessites are progressively heated is determined by the exchange cation (Table 3).

We also progressively heated birnessites of different origins to 200°, 400°, 600°, 800°, and 1000°C. The purpose here was to determine whether the formation conditions of the mineral are reflected in the heat-treated product.

TABLE 3. Major Crystal Phases Produced by Heating Synthesized Birnessites Saturated with Different Cations [13]

Saturating cations	Ionic radii of elements, Å	Phases determined at given temp., °C			
		200	400	600	800
K	1.33	Birnessite	Birnessite	Cryptomelane	Cryptomelane
Ba	1.34	Unordered birnessite	Hollandite	Hollandite	Hollandite
Sr	1.12	Unordered birnessite	"	"	"
Ni	0.69	Birnessite	Unordered birnessite	Bixbyite	Bixbyite
Mg	0.66	"	Unordered birnessite	Hausmannite	Hausmannite
Li	0.68	Unordered birnessite	Cryptomelane	Cryptomelane	"
Mn ²⁺	0.80	Unordered birnessite	Unordered birnessite	Bixbyite	Byxbyite

The samples were heated in a Silit [silicon carbide] muffle furnace at a heating rate of 5-10 deg/min.

The newly formed mineral phases were identified by x-ray diffraction analysis. The results are shown in Fig. 3, and Table 4 gives the interplanar spacings of the Debye diagrams and their magnitudes for some manganese and ferromanganese minerals taken from the American powder diffraction file [19].

We note that birnessites of the same type from different sites form identical new mineral phases in the transformation associated with heating.

In the temperature interval up to 400°C, the birnessite, regardless of origin, and the contaminant vernadite basically anamorphose (cf. Fig. 3, II).

When the hydrothermal birnessite is heated from 400 to 600°C, peaks appear in the diffractograms (cf. Fig. 3, III, a) indicating the formation of hausmannite (Mn₃O₄), which is in the tetragonal system. After the samples are heated to 800 and 1000°C, the hausmannite peaks (cf. Figs. 3, IV, a and V, a) become more distinct. This indicates that as the temperature is raised above 400°C, hausmannite first appears, and then its structure becomes more perfect.

Sedimentary birnessite undergoes different transformations. In the temperature range from 400° to 600°C, the diffractograms show two distinct phases, a manganese spinel of the cubic class, and hausmannite (cf. Fig. 3, III, b). As the temperature is raised from 600° to 1000°C, the spinel peaks on the diffractograms become noticeably larger and more distinct, while the hausmannite peaks diminish, and disappear at 1000°C (cf. Figs. 3, IV, a and V, a).

According to data reported in the literature, the hausmannite-spinel transition occurs around 1050-1070°C [11 and elsewhere], whereas the sedimentary birnessites from the macro-nodules from Pacific Ocean Stations 645 and 649 we studied transform to spinel at much lower temperatures.

Such behavior during heating by birnessites of different origins may be related to different contents of the elements present in them as isomorphic replacements, or to the different minerals closely associated with them genetically.

The analyses, as stated above (cf. Table 2), showed somewhat higher contents of iron in the marine than in the hydrothermal micronodules, since the marine nodules contain such iron-containing minerals as vernadite and hydrogoethite in addition to birnessite.

According to [15, 17, 20, and others], the iron in natural and synthetic manganese oxides facilitates their transformation to spinellike minerals when they are heated, but it is complex iron-manganese phases that form.

In the Fe₂O₃-Mn₂O₃ phase diagram (Fig. 4) taken from K. Ono et al. [7], which was obtained by heating chemically prepared mixtures, it can be seen that in the region where iron

TABLE 4. Interplanar Spacings d and Line Intensities I in X-Ray Diffraction Patterns of Manganese, Iron-manganese, and Iron Minerals

Hausmannite Mn_3O_4 (1-1127)		Manganese oxide (spinel) Mn_3O_4 (13-162)		Bixbyite $(Mn, Fe)_2O_3$ (8-10)		Jacobsite $(Mn, Fe)_2O_4$ (8-15)		Geothite $HFeO_2$ (8-97)		Magnetite Fe_3O_4 (11-614)		Hematite $\alpha-Fe_2O_3$ (15-534)		Maghemite $\gamma-Fe_2O_3$ (13-458)	
d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I
-	-	-	-	-	-	-	-	-	-	-	-	-	-	7,91	10
-	-	-	-	-	-	-	-	-	-	-	-	-	-	6,93	20
-	-	-	-	-	-	-	-	-	-	-	-	-	-	6,32	10
-	-	-	-	-	-	-	-	-	-	-	-	-	-	5,88	40
-	-	-	-	-	-	-	-	-	-	-	-	-	-	5,32	10
4,92	20	-	-	-	-	4,94	40	5,00	20	-	-	-	-	-	-
-	-	4,86	50	-	-	-	-	-	-	4,85	40	-	-	4,81	40
-	-	-	-	4,68	10	-	-	-	-	-	-	-	-	-	-
-	-	-	-	4,21	10	-	-	4,21	100	-	-	-	-	-	-
-	-	-	-	3,83	60	-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-	-	3,72	60
-	-	-	-	3,35	10	-	-	3,37	20	-	-	3,66	25	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-	-	3,39	60
3,08	31	-	-	-	-	-	-	-	-	-	-	-	-	3,19	30
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
-	-	2,98	50	2,99	30	3,01	40	-	-	2,96	70	-	-	2,94	90
2,87	8	-	-	-	-	-	-	-	-	-	-	-	-	2,77	30
2,75	63	-	-	2,72	100	-	-	2,69	8	-	-	2,69	100	2,70	90
-	-	-	-	-	-	-	-	2,57	20	-	-	-	-	2,63	30
-	-	2,54	100	2,51	20	2,56	100	2,51	100	2,53	100	2,51	50	2,57	20
-	-	-	-	-	-	-	-	-	-	-	-	-	-	2,51	100
2,48	100	2,43	10	-	-	2,45	3	2,48	70	2,91	10	-	-	2,40	20
2,36	13	-	-	2,35	40	-	-	-	-	-	-	-	-	2,30	20
-	-	-	-	2,21	20	-	-	2,25	20	-	-	-	-	2,24	10
-	-	2,10	50	2,11	10	2,12	40	2,18	40	2,096	70	-	-	2,16	10
2,03	15	-	-	2,01	40	-	-	2,00	10	-	-	2,01	30	2,08	90
-	-	-	-	1,92	10	-	-	-	-	-	-	-	-	-	-
-	-	-	-	1,87	40	-	-	-	-	-	-	-	-	1,81	80
1,79	18	-	-	-	-	-	-	-	-	-	-	1,63	40	-	-
1,70	5	1,71	20	1,72	25	1,73	10	1,719	50	1,71	60	-	-	1,69	40
1,64	5	-	-	1,65	90	-	-	1,689	20	-	-	1,69	60	1,66	10
-	-	1,62	50	1,61	20	1,64	60	-	-	1,61	85	-	-	1,63	10
1,57	50	-	-	1,56	20	-	-	-	-	-	-	1,594	16	1,60	90
1,50	50	1,49	50	1,53	30	1,50	60	-	-	-	-	-	-	1,54	20
1,47	3	-	-	1,48	20	-	-	-	-	1,48	85	1,48	35	1,52	20
1,44	8	-	-	1,45	30	1,43	5	-	-	-	-	1,45	35	1,47	90
-	-	-	-	1,42	80	-	-	-	-	-	-	-	-	-	-
1,38	4	-	-	1,38	40	-	-	-	-	-	-	-	-	-	-
-	-	1,28	20	-	-	-	-	-	-	-	-	-	-	-	-

Note. ASTM table values from [19] are given in parentheses.

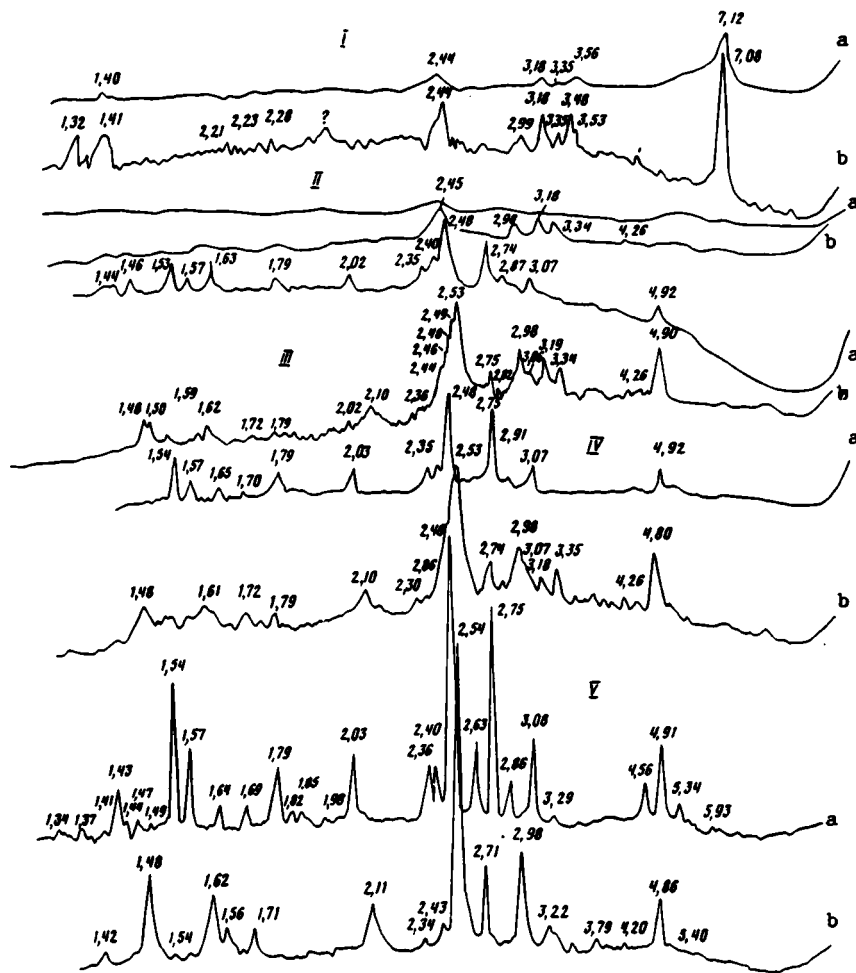


Fig. 3. Diffractograms of heat-treated birnessites. I-V - samples heated to, °C: I) 200; II) 400; III) 600; IV) 800; V) 1000 (a - hydrothermal; b - sedimentary).

strongly predominates over manganese, only hematite forms in the temperature region of interest to us. When the manganese content in the mixture increases, x-ray diffraction identifies two phases, hematite and bixbyite ($\text{Mn, Fe}_2\text{O}_3$), which increases with increasing manganese content. In the region of high (> 50%) manganese contents a spinel (jacobsite) forms at 950°C.

To test the possible effect of iron compounds on the pathway and rate of birnessite formation, the following mixtures were prepared: 1) hydrothermal birnessite and a sample of Fe-Mn crust, and 2) hydrothermal birnessite and x-ray amorphous iron oxides found in a fer-ruginous ooze. The combined study of the samples (chemical and x-ray analysis, electron diffraction, etc.) showed that the major mineral of the Fe-Mn crusts is Fe vernadite. It contains 11.1% iron and 15.3% manganese.

A sample of iron ooze collected from the bottom of Lake Nyal-Yavr on the Kola Peninsula contained 21.5% iron (total) and about 0.09% manganese.

The mixtures consisted of four parts by weight birnessite and one part Fe vernadite or iron oxyhydroxides. Small amounts of the mixtures of hydrothermal birnessite with vernadite and with the iron oxyhydroxides were thoroughly ground in an agate mortar until a fine dust was obtained, and then heated according to the program used for the hydrothermal and sedimentary birnessites.

When the mixture of hydrothermal birnessite and x-ray amorphous iron oxyhydroxides was heated to 1000°C, two mineral phases formed, hausmannite, the major form, and what is most likely bixbyite (Fig. 5a and Table 4).

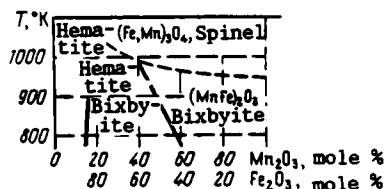


Fig. 4. Phase diagram of the system Fe_2O_3 - Mn_2O_3 [17].

The diffractogram for the mixture of hydrothermal birnessite and Fe vernadite heated to the same temperature is somewhat different. As can be seen from the data in Fig. 5b and Table 4, it is practically monominerallic hausmannite that forms. The very small peaks are possibly from a complex iron-manganese oxide.

For comparison we also heated a todorokite ore from the Charco-Redondo deposit in Cuba, which had a total of 4.2% iron oxides, 9.6% MnO , and 68.8% MnO_2 . It contained between 0 and 0.05% nickel, copper, and cobalt oxides [2]. The diffractograms of the starting sample of todorokite ore and of a sample heated to 1000°C are shown in Fig. 5c, d. They show that despite the presence of small amounts of iron in the sample, hausmannite is formed during heating.

The results obtained by heating hydrothermal minerals (todorokite and birnessite) in a mechanical mixture with iron compounds allow one to conclude that the iron compounds have no significant effect on transformations of manganese minerals.

Under these conditions it is natural to assume that the phase transitions are governed by the cations that enter the sedimentary birnessites as isomorphic replacements. In hydrothermal minerals, the cation composition of their layers is represented almost exclusively by manganese, while in sedimentary birnessites the cation composition has relatively elevated contents of nickel, copper, cobalt, manganese, and other elements. The presence of these isomorphic cations apparently leads to the transition of marine birnessite to spinel occurring at lower temperatures than in its hydrothermal analog. Energy-dispersive analysis of the chemical composition of individual particles of calcined birnessites confirms this conclusion. While the spectra of particles of hydrothermal birnessite show peaks only for manganese, the particles of the sedimentary sample also have strong peaks for cobalt and what are perhaps copper and other elements.

If this hypothesis is true, then other nonhydrothermal Fe-Mn minerals containing elevated concentrations of nickel, copper, and cobalt should also convert to a manganese spinel rather than to hausmannite after being heated to 1000°C .

To test the hypothesis, we heated several marine Fe-Mn nodules and crusts of hydrogenous origin that contained two orders of magnitude more nickel, copper, and cobalt than comparable marine formations of hydrothermal origin.

Then nodules were collected during Voyage 9 of the RV Dmitrii Mendeleev at Station 623 (Pacific Ocean) from two horizons: 0-2 and 265 cm, and at Station 2201-2 (Bauer depression, Pacific Ocean) during Voyage 24 of the RV Academician Kurchatov from the top section of the metalliferous sediments.

The Fe-Mn nodules from the 0-2-cm horizon at Station 623 contain about 16% iron and 14.1% manganese. Electron diffraction data show that these nodules consist of mixed-layer asbolite-buserite, Fe vernadite, and ferroxigite. The nodules at the 265 cm horizon contain about 17% iron and 12.8% manganese.

The nodules from the top of the metalliferous sediments at Station 2201-2 contain 10.5% iron and 16.9% manganese, and comprise vernadite, mixed-layer asbolite-buserite, and ferroxigite.

As can be seen from the diffractograms (cf. Fig. 5e-g), the major product formed by heating all three samples is a manganese spinel. Hematite is a secondary phase in the calcined samples from Station 623 (265 cm horizon).

* * *

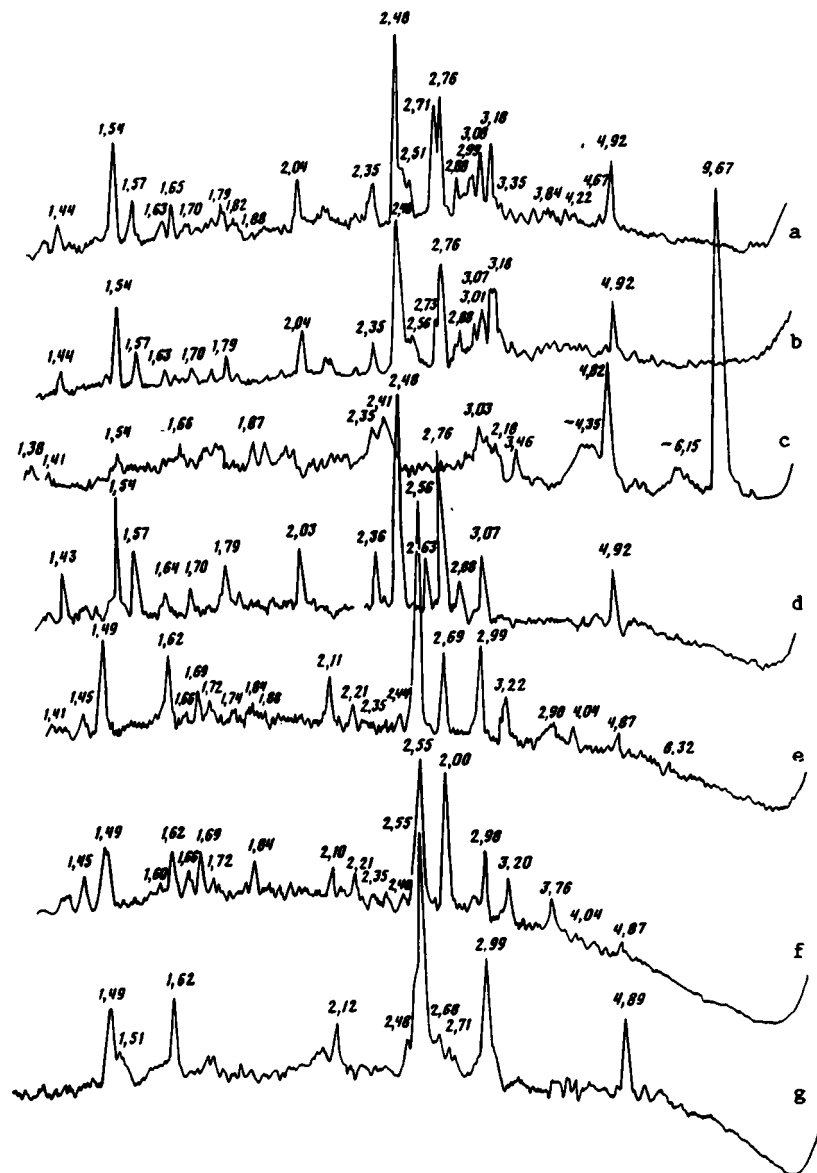


Fig. 5. Diffractograms of Fe-Mn nodules and other formations heated to 1000°C. a) Mixture of hydrothermal birnessite (four parts) and x-ray amorphous iron oxyhydroxides (one part); b) mixture of hydrothermal birnessite (four parts) and Fe vernardite (one part); c) todorokite ore (Charco-Redondo deposit, Cuba), original sample; d) the same, heated to 1000°C; e) Fe-Mn nodule (Station 623, Voyage 9 of the RV Dmitrii Mendeleev, 0-2 cm horizon; f) the same (collected at 265 cm horizon); g) Fe-Mn nodule from the top of metalliferous sediments (Bauer depression, Voyage 24 of the RV Akademichian Kurchatov).

The thermal treatment of birnessites of different origins has provided evidence that sedimentary birnessites convert to spinels at temperatures between 800-1000°C, while hydrothermal birnessites convert to hausmannite at these temperatures.

These results can be utilized as a supplementary criterion in addition to those previously proposed by E. Bonatti et al. [9], P. Rona [18], and others for determining the genesis of marine Fe-Mn crusts and nodules.

LITERATURE CITED

1. V. A. Drits, V. V. Petrova, A. I. Gorshkov, et al., "Manganese minerals of Fe-Mn micro-nodules in the sediments of the Central Pacific Ocean and their postsedimentary transformations," *Litol. Polezn. Iskop.*, No. 3, 17-39 (1985).
2. E. A. Sokolova, *Manganese Volcanosedimentary Formations* [in Russian], Nauka, Moscow (1982).
3. V. F. Chukhrov, A. I. Gorshkov, and V. A. Drits, "Advances in the crystal chemistry of manganese oxides," *Zap. Vses. Mineral. O-va*, 116, No. 2, 210-221 (1987).
4. F. V. Chukhrov, A. I. Gorshkov, E. S. Rudnitskaya, et al., "Toward the characterization of birnessite," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 9, 67-76.
5. F. V. Chukhrov, B. A. Sakharov, A. I. Gorshkov, et al., "Structure of birnessite from the Pacific Ocean," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 8, 66-73 (1985).
6. L. E. Shterenberg, V. A. Aleksandrova, I. F. Gablina, et al., "Composition and structure of manganese crusts from the Sea of Japan," *Tikhookean. Geol.*, No. 1, 125-128 (1986).
7. L. E. Shterenberg, V. A. Aleksandrova, A. V. Sivtsov, et al., "Composition, structure, and distribution of Fe-Mn micronodules in the sediments of the northeast Pacific," *Litol. Polezn. Iskop.*, No. 6, 58-70 (1985).
8. L. E. Shterenberg, M. P. Antipov, A. Ya. Il'ev, et al., "Ferromanganese formations of the Sea of Okhotsk," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 12, 106-115 (1987).
9. E. Bonatti, T. Kramer, and H. S. Rydell, "Classification and genesis of submarine iron-manganese deposits," in *Ferromanganese Deposits on the Ocean Floor*, Lamont-Doherty Geol. Observatory and IDOE-NSF (1972), pp. 149-166.
10. I. Corliss, M. Lyle, I. Dymond, et al., "The chemistry of hydrothermal mounds near the Galapagos Rift," *Earth Planet. Sci. Lett.*, 40, No. 1, 12-24 (1978).
11. G. M. Fauling, W. K. Zwickler, and W. I. Forgeng, "Thermal transformation and properties of cryptomelane," *Am. Mineral.*, 45, No. 9/10, 939-946 (1960).
12. R. Giovanoli, E. Stahei, and W. Feitknect, "Über oxydroxide des Vierwertigen Mangans mit Schichtengitter, Mitteilung: Mangan(III)-Manganat(IV)," *Helv. Chim. Acta*, 53, 453-464 (1970).
13. E. D. Glover, "Characterization of a marine birnessite," *Am. Mineral.*, 62, No. 3-4, 278-285 (1977).
14. D. C. Golden, I. B. Dixon, and C. C. Chen, "Ion exchange thermal transformations and oxidizing properties of birnessite," *Clay Min.*, 34, No. 5, 511-520 (1986).
15. I. S. Huebner, "The manganese oxides: A bibliographic commentary," *Reviews in Mineralogy* (1981), Vol. 3, pp. SH-1 to SH-17.
16. P. Lonsdale, V. M. Burns, and M. Fisk, "Nodules of hydrothermal birnessite in the caldera of a young seamount," *J. Geol.*, 88, No. 5, 611-618 (1980).
17. K. Ono, T. Ueda, T. Ozaki, et al., "Thermodynamic study of the iron-manganese-oxygen system," *Nippon Kinzoku Gakkaishi*, 36, 757-763 (1971).
18. P. A. Rona, "Criteria for recognition of hydrothermal mineral deposits in oceanic crust," *Econ. Geol.*, 73, No. 2, 135-160 (1978).
19. *Selected Powder Diffraction Data for Minerals*, JCFDS (1974).
20. H. I. Van Hook and M. L. Keith, "The system $\text{Fe}_2\text{O}_3\text{-Mn}_3\text{O}_4$," *Am. Mineral.*, No. 1, 69-83 (1958).

FERROMANGANESE CRUSTS AND NODULES IN THE KURILE ISLAND ARC:
STRUCTURE, COMPOSITION, AND ORIGIN

T. Yu. Uspenskaya, A. I. Gorshkov,
G. M. Gavrilenko, and A. V. Sivtsov

UDC 553.32(571.66)

Detailed studies have been carried out on the structure and composition, both mineralogical and chemical, of ferromanganese crusts and nodules on submarine volcanoes in the Sea of Okhotsk, near the islands of Simushir, Chernye Brat'ya, and Brouton. On the basis of a number of mineralogical and chemical characteristics, it is concluded that the crusts and nodules studied are mainly of hydrothermal-sedimentary origin. During the last stages of formation, they experienced hydrogenic and diagenetic introduction of ore components, as well as post-sedimentational microbiological alteration of the manganese minerals.

There currently is a wide literature on ferromanganese nodules in the oceans of the world. Studies relating to the composition, structure, and distribution of nodules on island arcs are relatively few, however. For example, about the only papers on the Kurile island arc are [5, 10, 11], which present the results of investigations into the morphology and chemical composition of Fe-Mn deposits. This information is obviously inadequate for a complete characterization of the ore deposits of the region, not to mention determination of their origin.

A considerable amount of data has been accumulated in the literature so far documenting the significant role of island-arc volcanism in the supply of ore elements into the ocean, from both terrestrial and submarine volcanic and hydrothermal activity. However, even to guess the approximate scale of this activity at present is complicated, because of the relatively small amount of direct observations of submarine gasohydrothermal activity in modern island arcs. And it is probably quite significant, since a great amount of geological and historical geology data attests to the broad scale of this process in ancient and modern arcs, where exhalation-hydrothermal ore deposits are concentrated [8, 9].

In this connection, a considerable amount of information on modern island arcs comes from indirect observations, among which studies in marine geology are quite valuable, especially sampling in the area of submarine volcanoes.

Material and Methods. The Fe-Mn nodules and crusts from the Kurile region that were studied were obtained during the 15th (1982) and 17th (1983) voyages of the research vessel "Volcanolog" (Fig. 1). Geological sampling (dredging) was carried out on the crests of submarine volcanoes and volcanic ridges. Rocky material, including angular blocks and fragments of mainly andesitic volcanic rock, were brought up from the submarine volcanoes Vavilov (B15-87), Arkhangel'skii (B15-91), Obruchev (B17-8, 9, 10, and 11), and an underwater ridge (B17-44, 45 and 46) located around the islands of Simushir, Chernye Brat'ya, and Brouton (see Fig. 1). The dredging also produced more basic (basalts, andesitic basalts) and more acidic (dacites, andesitic dacites) varieties of volcanites. The material dredged from volcanoes on the Sea of Okhotsk side of the islands of Urup and Iturup (B17-15, 16, 17, 20, 23, 25, 38, 40, 41, 43) also consisted mainly of unrounded blocks and fragments of various volcanic rocks (from basalt to rhyolite). These rocks commonly have the globular or pillow structure, fresh appearance, and traces of recent hydrothermal activity (sulfur-filled joints, etc.) that are typical of submarine eruptions.

The sampling at virtually all stations brought up ferromanganese deposits of various types: nodules (at sta. B15-87, B17-41, 44, and 46) and crusts (at sta. B15-87, 91, B17-8, 10, 15, 16, 17, 20, 23, 38, 43, and 46). Moreover, at sta. B17-20 slabs of clastic rocks

Institute of the Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Academy of Sciences of the USSR, Moscow. Institute of Oceanology, Academy of Sciences of the USSR, Moscow. Institute of Volcanology, Far-Eastern Branch, Academy of Sciences of the USSR, Petropavlovsk-Kamchatskii. Translated from *Litologiya i Poleznye Iskopaemye*, No. 4, pp. 30-40, July-August, 1989. Original article submitted on June 20, 1988.

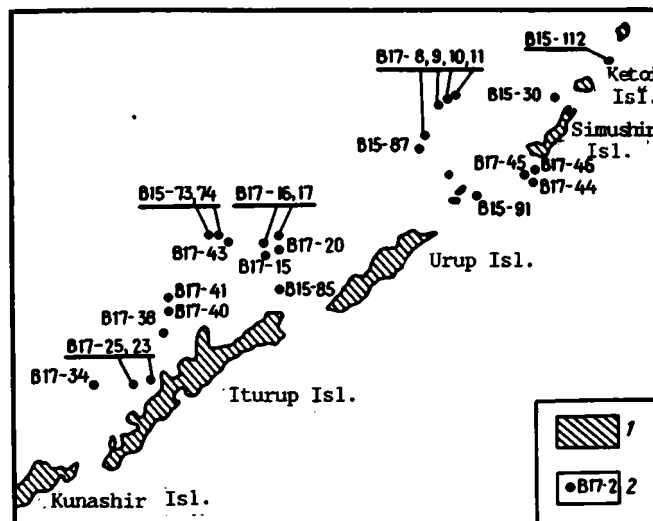


Fig. 1. Locations of stations where samples of ferromanganese deposits were obtained. 1) study area, 2) stations, with numbers.

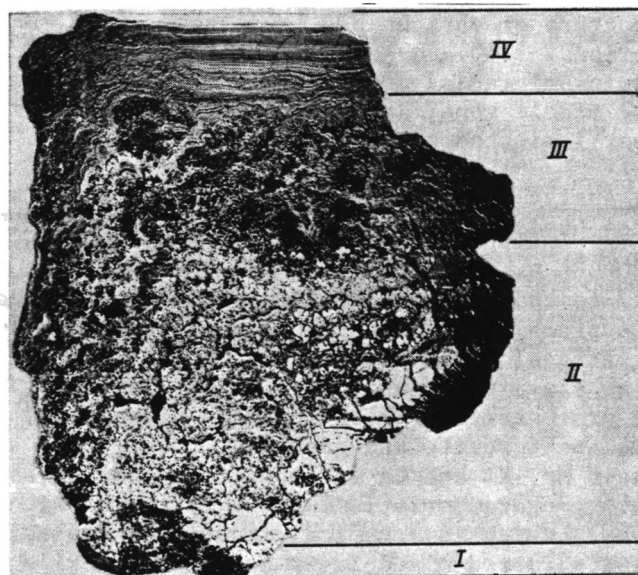


Fig. 2. Internal structure of a manganese crust (sta. B17-46); I-VI are zones. Polished section, $\times 2.5$.

(sandstone and conglomerate) cemented with iron and manganese hydroxides were hauled up. Also obtained were pumice and, at nearly every station, fossil material impregnated with ferromanganese hydroxides.

Study of the internal structure of the crusts and nodules, as well as determination of the optical properties of the mineral phases (reflectance and the presence or absence of anisotropy), were carried out by means of polished sections in reflected light. A number of methods were used to identify all minerals present in the ore material. Buserite-I was recognized by means of x-ray diffractometry of heated (100°C for 1 h) and unheated samples (DRON-1, Co K_{α} -radiation, 24 kV, 3 mA) [14]. Reliable identification of the rest of the Mn and Fe minerals was accomplished by means of analytical electron microscopy (microdiffraction of electrons and x-ray energy-dispersive microprobe analysis). The samples were analyzed on a JEM-100C electron microscope with energy dispersive attachment KEVEX-5100. Electron-microscope identification of minerals was done using the microdiffraction indices described in the literature [15-18 and others].

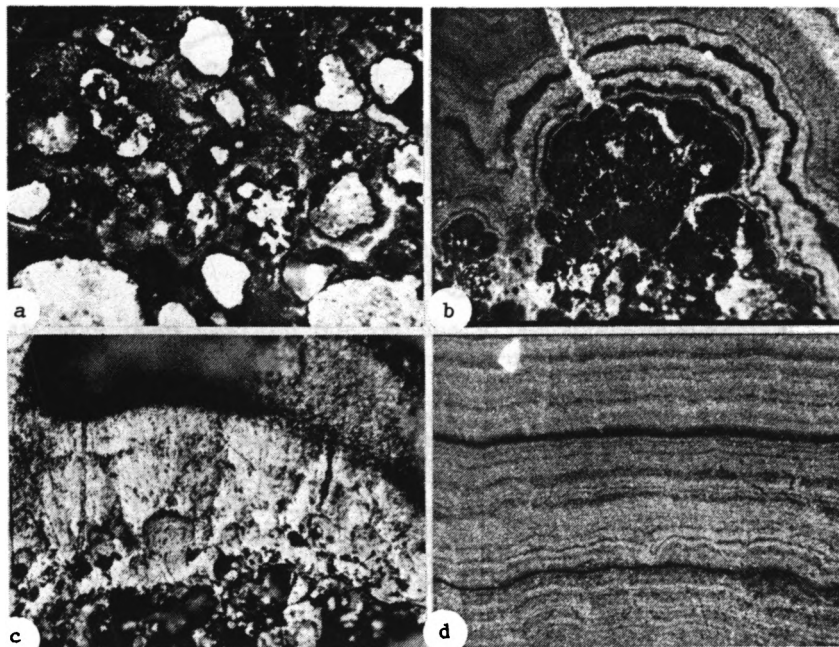


Fig. 3. Structure of various ore crust zones (sta. B-17-46); polished sections, $\times 140$. a) Basal layer; b) middle zone (black, globules of radial-dendritic texture; gray, cementing material); c) middle zone: columnar-fibrous todorokitic aggregate; d) upper laminated zone.

Results of Mineralogical Analysis. The ferromanganese ore materials studied can be subdivided into three types on the basis of external macroscopic features, internal structure, and mineralogical composition.

The first type (sta. B-17-44 and B17-46) includes crusts and nodules that are black in color with a lumpy or smooth surface, are composed of manganese hydroxides, and have a complex internal structure (Fig. 2). A basal layer is generally found in the lower part of the crust (Fig. 3a): rounded and angular clastic grains (0.5-2 mm in size) that are cemented with highly reflective anisotropic ore material, which includes birnessite, lesser amounts of vernadite, rare particles of asbolane-buserite and goethite. Microprobe analysis has shown that birnessite and vernadite contain Mg, K, and Ca as impurities, and in asbolane-buserite there is even Al (and sometimes Si). A characteristic feature of the chemical composition of these minerals is their lack of nickel, which is a typical impurity in pelagic ferromanganese nodules [13, 14, 17]. Moreover, disordered mixed-layer asbolane-buserite is one of the ore minerals of highly manganese-rich oceanic nodules [13, 19], while it is rarely encountered in crusts and nodules of the Kurile arc.

Over the basal layer a thick (3 cm) crust is developed (see Fig. 2, zone II), composed of slightly anisotropic globules (0.5-2 mm in diameter) of radial-dendritic texture, cemented with a dense, anisotropic laminated material (see Fig. 3b). A fresh surface of the cementing material is steel gray and has a metallic luster. Locally massive beds have a columnar-fibrous texture, which is typical of todorokitic aggregates (see Fig. 3c). Such textures have been noted previously in manganese crusts in the Sea of Japan [12, 22]. The globules are characteristically black with a dull luster. They are composed of finely dispersed aggregates of birnessite and vernadite with small amounts of platy particles of disordered todorokite, partially vernaditized. All of the minerals observed have the same chemical compositions, similar to that of birnessite and vernadite in the basal layer. It should be pointed out that the vernadite studied contains no iron (Fig. 4), which always accompanies the mineral in marine deposits. Iron-free vernadite has been discovered in natural marine deposits for the first time. Judging by the similarity in chemical composition of the first time. Judging by the similarity in chemical composition of the iron-free vernadite, birnessite, and todorokite, it is assumed that the vernadite formed in the post-sedimentational stage as a result of alteration of birnessite and todorokite due to the action of manganese-oxidizing bacteria. The possibility of such transformations in the case of todorokite has been shown experimen-

tally [18]. Electron-microscope indicators of this process have been discussed in detail in [15].

The vernaditization of todorokite is more distinctive, and is far more easily shown, because the shape of todorokite grains differs sharply from the form of vernadite aggregates. This is even shown by electronogram. In the case of birnessite, it is difficult to judge just how strongly it is affected by vernaditization, since the critical reflections of vernadite and birnessite fall on top of one another, and the presence of birnessite can be determined only by the basal reflection with $d_{001} = 7.1/2 \text{ \AA}$. It is hard to explain direct precipitation of vernadite. It is known [15] that for rapid deposition of vernadite from solutions containing Mn^{2+} a very strong oxidizing agent is needed, which is lacking under natural conditions of discharge of hydrothermal solutions (the oxidizing capacity of seawater enriched in oxygen is insufficient for crust formation that is so rapid, judging by the thickness of the layer).

The chief ore-forming mineral in the cement is platy birnessite, which is very highly recrystallized and ordered, and gives a diffraction pattern of not only the pinacoidal (hk0) and basal (00 ℓ) reflections but also (hk ℓ). Disordered todorokite, partially altered to iron-free vernadite, is also seen in lesser amounts. Compared to the previous samples, the impurities in the birnessite and todorokite cement are unchanged.

A completely friable zone lies above with a sharp contact (see Fig. 2, zone III). This zone is composed of an aggregate of fine, branching dendrites, partly cemented by dense, massive material that is identical in character and mineralogy to the cement in the basal and globular layers. Microdiffraction of the fine dendrites showed that they are composed mainly of 14 $\text{\AA}$ birnessite and todorokite. Three varieties of todorokite were noted in electron microscope preparations: disordered, and with a_0 equal to 9.75 and 19.5 $\text{\AA}$. The first is most common. On electronograms, 14 $\text{\AA}$ birnessite commonly lacks the weak diffusion lines, typical of disordered todorokite, which are apparently present in fine epitaxial growths with 14 $\text{\AA}$ birnessite parallel to the pinacoidal plane. A distinguishing feature of the chemical composition of 14 $\text{\AA}$ birnessite and todorokite in the friable zone is the absence of Mg in some grains. K and Ca are always present. This mineral association is absolutely not found in pelagic Fe-Mn nodules and hydrogenic crusts. 14 $\text{\AA}$ birnessite has previously been found in micronodules in coccolith muds near the transform fault Atlantis (Atlantic Ocean) [16] and in hydrothermal manganese crusts in the Tadzbur rift [5].

In a sample from sta. B17-46 the upper part of the crust is concealed by a thick (8 mm), dense, finely laminated layer (see Fig. 2, zone IV) with a very smooth surface (see Fig. 3d). The laminated texture is due to interbedding of thin black and thicker steel-gray layers. The mineralogical composition of the upper bedded unit is like that of the cementing material in the underlying zone.

Ellipsoidal nodules (5 $\times$ 3.5 cm) brought up from sta. B17-44 have a rough, irregular surface and a concentrically zoned structure (Fig. 5), caused by interlayering of globular-dendritic, weakly reflecting to nearly isotropic material with thinly layered collomorphic zones in which the ore is more highly reflective and distinctly anisotropic. In their optical properties, physical features (color, luster), and mineralogical composition the globular-dendritic layers are identical to globular crusts described above, while the thinly layered zones are like the cementing material in the upper layers of the unit.

The second type includes crusts, formed from sediment, which are composed mainly of green and yellowish-green clay, brown Fe-Si veins, and manganese hydroxides (sta. B15-87; B17-9, 10, 11, 17, 25).

The green and yellowish-green clay forms either dense masses with conchoidal fracture, cementing angular and poorly rounded clasts of sediment, or friable bedded deposits. On surfaces and along fractures, the greenish-yellow clay is often a brownish-ocher in color. According to x-ray data, the green clay is composed of nontronite. Microprobe analysis of individual particles of this mineral showed that it contains Fe, Si, and a small amount of K. In some particles there are minor amounts of Ca, Mg, and Al. In samples of the brownish-ocher material, particles of poorly ordered ferroxhyte (δ' -FeOOH) were found, which explains the color. The gradual transition in color (from yellowish-green to brown) on the surface of the crusts and in fractures, as well as the absence of manganese in the ferroxhyte, which is normally present in the mineral when it is hydrogenically deposited [14], suggest that the ferroxhyte was formed in the post-sedimentational stage during alteration of clayed material in an oxidizing environment of bottom waters.

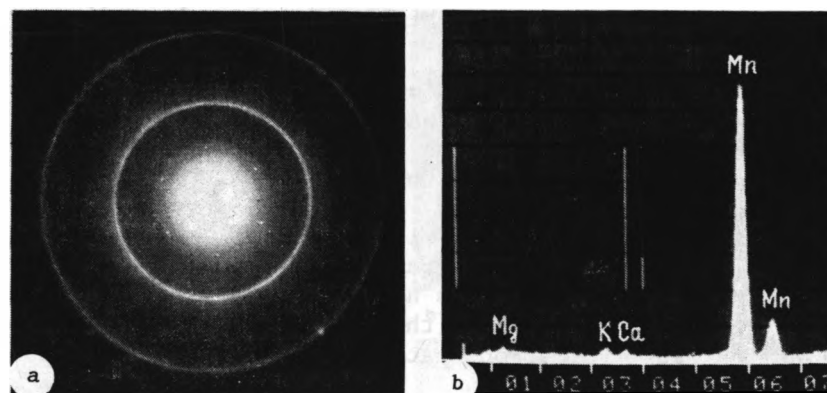


Fig. 4. Electronogram (a) and energy dispersive spectra (b) of iron-free vernadite

Friable nontronitic clay (sta. B17-9, 10, 11) is full of sparse, thin brown veinlets that have a conchoidal fracture and glassy luster. They are composed of an amorphous, gelatinous, glasslike Fe-Si material with minor amounts of poorly ordered ferroxhyte (without Mn). All of the reflections on the electronogram have a diffusive character. The very latest mine alization is represented by development in the entire crust of massive (up to 1.5 mm) birnessitic interbeds that transect the Fe-Si veinlets and branch into thin dendrites composed of birnessite with minor disordered todorokite. In addition, manganese hydroxides form thin platelets on clastic grains and foraminifera tests.

Dense nontronitic crusts have numerous fractures that are filled with massive black (on steel-gray fracture surfaces) Mn hydroxides, which occur as very fine dendritic intergrowths within the clay mass as well. Mineralogically, the massive manganese interbeds are composed of todorokite (disordered and with $a_0 = 9.75 \text{ \AA}$) and platy $7 \text{ \AA}$ birnessite with minor amounts of $14 \text{ \AA}$ birnessite and iron-free vernadite. All of the phases have the same cation impurities (K, Ca, Mg). Mg is absent from particles of well ordered todorokite. Some particles of disordered todorokite are replaced by iron-free vernadite, while a few particles that appear to be todorokite have a diffraction pattern typical of birnessite.

The third type includes crusts and nodules that contain Mn and Fe hydroxides (sta. B15-91; B17-15, 16, 20, 23, 38, 40, 41, 43), the lower part of the thickest crusts (B17-15 and B17-43) are sediments whose grains are cemented with massive, black Mn hydroxides with a fresh surface that is steel-gray with a metallic luster. They are composed mainly of birnessite and todorokite (disordered and with $a_0 = 9.75 \text{ \AA}$) with a small amount of $14 \text{ \AA}$ birnessite and iron-free vernadite. Todorokite is commonly found with intergrowths of $14 \text{ \AA}$ birnessite. A few particles of todorokite are partially vernaditized. The chemical composition of the todorokite is no different from the manganese minerals in the types of crust described above.

The upper part of these crusts differs from the lower in the presence of thin laminations caused by the intercalation of brown ore and light-colored clay layers. The ore is characterized by a resinous luster on fresh surfaces. It has a low reflectance (dark-grey compared to the light-gray manganese layers) and is isotropic under crossed nichols. The ore occurs in the crust in the form of thin collomorphic interbeds and thicker layers with an acircular to dendritic texture. Similar textures are present in pelagic hydrogenic crusts [6] and sedimentational nodules [14]. According to electron microdiffraction, the interbeds are composed of fine platy aggregates of Fe-vernadite, Mn-ferroxhyte, and angular masses of goethite with sparse, finely dispersed segregations of ferriiferous x-phase. On the basis of the mineral association and the composition of cation impurities (Si, Mg, Al, K, Ca) the ore material of the finely laminated part of the crust is similar to that of oceanic nodules that are enriched in iron ($\text{Mn/Fe} < 2.5$) [14]. Crusts of the third type differ in chemical composition of Fe-vernadite and Mn-ferroxhyte by an enrichment in phosphorous and barium. In some crusts (sta. B16-17), which are apparently marginal areas in contact with sediments, there are highly reflective, anisotropic dendritic interbeds which consist of asbolane-buserite, buserite-I, birnessite, and lesser amounts of disordered todorokite and buserite-II. A characteristic feature of the composition of asbolane-buserite, birnessite, buserite-II and probably buserite-I altered to birnessite in the electron microscope vacuum, is the presence of nickel. Similar interlayers were found in donut-shaped nodules (sta. B-17-41): a

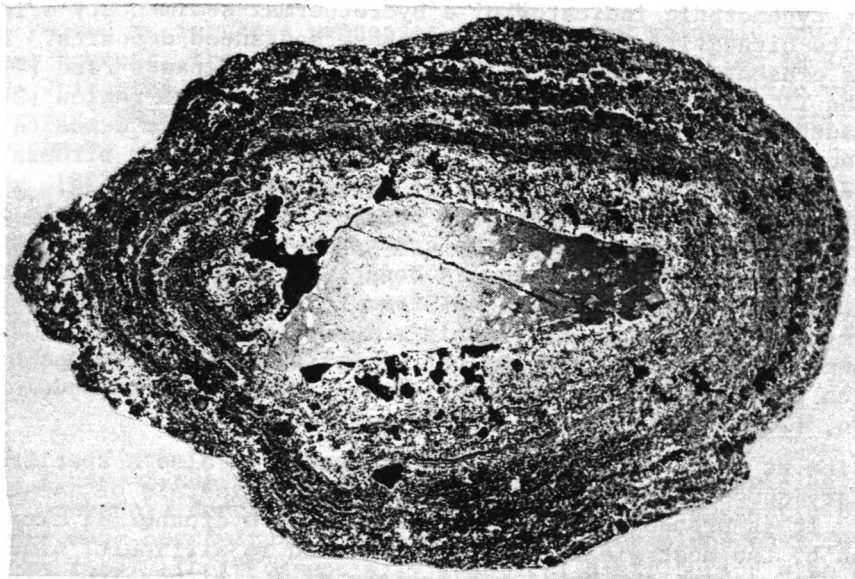


Fig. 5. Concentrically zoned structure of ore nodule (sta. B17-44. Polished section, $\times 2.1$.

film of ring-shaped ore growing over the sides of a large pebble (2 cm across), with the center above and below not covered with the film and in contact with sediments and bottom water. Such nodule forms, characteristic of diagenetic ferromanganese nodules in lakes and marginal seas, are produced by diagenetic mobilization of ore components from the underlying reduced sediments [20].

The results of chemical analysis of the samples studied has been presented earlier in [4]. The total content of ore elements in the nodules and crusts of the Kurile arc ranges from 7 to 40% by weight. The manganese concentration varies from hundredths of a percent of a percent to 39% (average 11.3%), and iron from tenths of a percent to 27% (average 13%). This variability in the macrocomponents is also reflected in the value of the manganese modulus (Mn/Fe), which has a wide range: from 0.002 to 122.

As for the minor ore elements, their content is lower than in nodules and crusts in the pelagic areas of the ocean [11]. The average value of cobalt in ferromanganese concretions in the Pacific is 0.33%, while the average in our samples is 0.037%; for nickel these figures are 0.59 and 0.086%, and for copper, 0.38 and 0.011%. Only for zinc was the average concentration in our samples close to that in pelagic nodules and crusts: 0.065 and 0.084%, respectively.

The low concentration of minor elements in the ferromanganese deposits of the Kurile Islands supports the suggestion that nodules and crusts of the peripheral parts of the ocean are depleted in ore microelements [11].

Discussion of Results. A number of features identified as a result of the mineralogical investigation of the nodules and crusts of the Kurile region support a hydrothermal-sedimentary origin for the first two types of ore deposits and the lower part of the third. This mainly applies to the fractionation of Fe and Mn, which appear as pure iron and pure Mn phases which formed in the following sequence: first Fe silicate (nontronite) was deposited, areas of which were then impregnated with manganese hydroxide. The association of green nontronitic clay with massive manganese crusts is typical of hydrothermal ferromanganese deposits of the Galapagos rise [7, 26, 28], the TAG ore district on the Mid-Atlantic ridge [30], the Explorer Ridge near the Pacific spreading center [24], and others. The separation of Fe and Mn taken place as a result of changes in the Eh of hydrothermal solutions under near-surface conditions, to the extent that they are diluted with normal seawater. Harder has shown in [25] that the synthesis of nontronite is controlled by both Eh and the concentration of Fe^{2+} and Si in solution. Iron will thus precipitate under more reducing conditions than manganese, and the formation of nontronite precedes that of manganese hydroxides.

Another important typomorphic indicator of a hydrothermal-sedimentary origin of these crusts is the todorokite-birnessite composition of these manganese deposits. This manganese mineral association is present in hydrothermal crusts of the Galapagos rise [7, 26, 28], Explorer Ridge [24], the TAG ore field [30], the Tonga-Kermadoc Ridge region [27], the Sea of Japan [12, 22], the Tadzhur rift [5], and others. Many manganese ore deposits in the regions listed above are characterized by predominance of either todorokite or birnessite. For example, crusts in the TAG ore field have a chiefly birnessite composition [30], while crusts on the submarine seamounts Tarasov and Bezymyanii in the Sea of Japan are mainly todorokite [12]. On the basis of average mineral composition, the crusts of the Kurile region can be considered birnessitic. This mineral is often found in oceanic ferromanganese nodules that have been enriched in manganese. However, it does not form thick masses in them, and is mainly the result of the aging of ore material originally composed of busserite-1 [13]. Incidentally, the latter was not found in crusts and nodules of types I and II or in manganese cement in the lower part of thick type III crusts. Todorokite is rarely found in nodules of sedimentary-diagenetic origin, [21, 29].

The 14 Å birnessite we observed in Type I and II crusts is also a specific mineral in hydrothermal-sedimentary deposits, one of the characteristic minerals of manganese crusts of the Tadzhur rift [5]. It is probably present in other known hydrothermal crusts as well, but its identification by the most widely used x-ray method is difficult, since the intensive 14 Å reflection is identical with the usual reflections of 7 Å birnessite. The identification of 14 Å birnessite by the electron microdiffraction method is very easy, however, as a result of the presence of a network of weak and strong reflections distributed according to the pseudohexagonal law [16].

Another important indicator of a hydrothermal origin is the depletion in the principal manganese minerals of nickel (0.0n%) and apparently copper and cobalt as well, as shown by chemical analysis of the crust (semiquantitative determination of Cu and Co in individual manganese mineral grains by energy dispersive microprobe analysis is very difficult). This is especially important in ordinary 7 Å birnessite. Unlike todorokite and 14 Å birnessite, it is commonly found in pelagic ferromanganese nodules of the diagenetic type. It is a product of the dehydration of busserite-I and always contains observable (> 1%) nickel and copper as impurities [13].

Finally, as of the type I and II ore deposits and the lower part of type III crusts enriched in manganese: the lack of distinct layering, the massiveness and thickness of the manganese accumulations, all set them apart from sedimentational-diagenetic ferromanganese deposits and are a consequence of rapid precipitation of manganese from solution.

Type III crusts and nodules have a more complex origin, the lower part, enriched in manganese, has all of the characteristics of a hydrothermal origin. The upper thinly laminated part of the crust has aspects of waning activity of a hydrothermal source and predominance of a hydrogenic supply of ore components. This is suggested by a close association between Fe and Mn hydroxides, appearing as Mn-feroxyhyte, and the presence of such features of sedimentational and diagenetic Fe-Mn ore minerals as x-phase, Fe-vernadite, asbolane-busserite, busserite-I, and busserite-II [13, 14] and the enrichment of the last three minerals in nickel.

In order to try to unite all three types and analyze the interrelationship of the various mineral phases and their combinations in space and time, the following scheme of mineral deposition during the evolution of hydrothermal solutions (their mixing with seawater, changes in Eh and pH, and their gradual discharge) must be considered. Near the surface, low-temperature acid solutions containing Fe^{2+} , Mn^{2+} , and Si react with seawater. The pH and Eh then increase and Fe and Si begin to precipitate as nontronite. Further oxidation of the solutions leads first to the oxidation of Fe^{2+} to Fe^{3+} and the formation of Fe-Si glass-like veins and then to precipitation of Mn in the following sequence: todorokite - todorokite + 14 Å birnessite - 7 Å birnessite. This sequence has been determined by the observed interrelationships of the mineral phases and is actually a general trend in which there are various departures (for example, the formation of birnessite globules in the crust at sta. B17-46 before the precipitation of todorokite and 14 Å birnessite), apparently associated with local variations in the physico-chemical conditions. After cessation of the hydrothermal activity, the effects of hydrogenic (the formation of Fe-vernadite and Mn feroxyhyte) and diagenetic (precipitation of asbolane-busserite and busserite-I enriched in nickel) additions to the ore components appear, as well as post-sedimentational processes of microbiological alteration of

manganese minerals (vernaditization of todorokite and 7 Å birnessite). It is not ruled out that the source of Fe and Mn in these processes is submarine volcanic and hydrothermal activity. In this case, however, the route to the place of precipitation is longer and passes through seawater in which the conditions are favorable for the formation of fine intergrowth of Mn and Fe hydroxides. Moreover, a longer exposure of the mineral particles to seawater promotes their enrichment in cation impurities.

Data on the chemical analyses of the ferromanganese crusts and nodules studied, presented in [4], also argue in favor of a predominantly hydrothermal origin. This conclusion is based firstly on the wide variation in the manganese modulus, which is a characteristic feature of regional development of submarine exhalation-hydrothermal processes [2, 3, 11], and secondly, on the low sedimentational-diagenetic Fe - Mn ore content of minor elements (Co, Ni, Cu) compared to oceanic ores, as a result of which the point corresponding to their composition on the triangular diagram Fe-Mn-(Ni + Co + Cu) $\times 10$ [23], falls in the zone of hydrothermal formation (or very near it).

* * *

Results of the study of the morphology, internal structure, mineralogy, and chemical composition of ferromanganese deposits of the Kurile island arc suggest a predominantly hydrothermal origin (hydrogenic precipitation of ore material took place only during the last stages of their formation). Their essentially identical distribution with the region of active volcanoes (as a whole) and with actual submarine volcanoes (in part) supports the suggestion of Avdeiko and Krasnov [1] that submarine hydrothermal activity is widespread in the region.

It is important to note that iron and manganese are extreme end members of a series of ore elements from hydrothermal solutions during marine volcanic - sedimentary formation: Cu-Cu, Zn-Zn, Pb-Ba-Fe-Mn [19]. Therefore ferromanganese nodules and crusts as a final substrate of submarine hydrothermal activity do not characterize it completely. The process of volcanic-sedimentary ore formation is more important than can be supposed on the basis of only the results of sampling and study of ferromanganese deposits in the region.

LITERATURE CITED

1. G. P. Avdeiko and S. G. Krasnov, "Sulfide ores and their association with submarine volcanoes and hydrothermal sources in island arcs," *Vulkanol. Seismol.*, No. 4, pp. 26-30 (1985).
2. G. N. Baturin, *Geochemistry of Ferromanganese Nodules in the Oceans* [in Russian], Nauka, Moscow (1986).
3. G. M. Gavrilenko, "Submarine volcano Esmeralda and associated ferromanganese ore deposits," *Vulkanol. Seismol.*, No. 1, pp. 51-55 (1981).
4. G. M. Gavrilenko and S. V. Khramov, "Ferromanganese deposits on the slopes of the Kurile island arc," *Vulkanol. Seismol.*, No. 2, 97-100 (1986).
5. A. I. Gorshkov, O. A. Bogdanova, and A. V. Sivtsov, "Petrography and mineralogy of ore deposits in the Tadzhur rift," in: *Geology of the Tadzhur Rift* [in Russian], Nauka, Moscow (1987), pp. 299-306.
6. I. O. Murdmaa and N. S. Skorniyakova (eds.), *Ferromanganese Nodules in the Central Pacific* [in Russian], Nauka, Moscow (1986).
7. Yu. M. Lazur, I. M. Barentsov, and V. V. Ermilov, "Dispersion of Mn-Fe-Ti-Cu-Zn mineralization in hydrothermal and pelagic sediments of the Galapagos rift zone (70th voyage of the drilling vessel "Glomar Challenger")," *Geokhimiya*, No. 2, pp. 170-177 (1986).
8. A. Mitchell and M. Garson, *Global Tectonic Position of Mineral Deposits* [in Russian], Mir, Moscow (1984).
9. L. N. Ovchinnikov, "Some patterns of volcanic ore formation," *Vulkanol. Seismol.*, No. 4, 36-47 (1981).
10. A. A. Orlov, *Forms of Ferromanganese Deposits in the Sea of Okhotsk*, in: *Geology of the Okhotsk Region* [in Russian], Izd-vo DVNTs Akad. Nauk SSSR, Vladivostok (1982), pp. 101-106.
11. N. S. Skorniyakova, "Chemical composition of ferromanganese nodules in the Pacific Ocean," in: *Ferromanganese Nodules in the Pacific Ocean* [in Russian], Nauka, Moscow (1976), pp. 190-240.
12. N. S. Skorniyakova, G. N. Baturin, E. G. Gurvich, et al., "Ferromanganese crusts and nodules in the Sea of Japan," *Dokl. Akad. Nauk SSSR*, 293, No. 2, pp. 430-434 (1987).

13. T. Yu. Uspenskaya, A. I. Gorshkov, and A. V. Sivtsov, "Mineral composition and internal structure of ferromanganese nodules from the Clarion-Clipperton fracture zone," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 3, 91-100 (1987).
14. T. Yu. Uspenskaya, A. I. Gorshkov, and A. V. Sivstov, "Internal structure and mineralogical composition of oceanic nodules of the sedimentational type," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 4, 88-97 (1988).
15. F. V. Chukrov, A. I. Gorshkov, E. S. Rudnitskaya, et al., "Vernadite," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 6, 5-19 (1978).
16. F. V. Chukrov, A. I. Gorshkov, A. V. Sivtsov, and V. V. Berezovskaya, "New mineral phases in oceanic manganese micronodules," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 1, 83-90 (1979).
17. F. V. Chukrov, A. I. Gorshkov, A. V. Sivtsov, and V. V. Berezovskaya, "Textural varieties of todorokite," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 12, 86-95 (1978).
18. F. V. Chukrov, A. I. Gorshkov, A. V. Sivtsov, and G. A. Dubinina, Biogenic Formation of Vernadite-Feroxyhyte Associations [in Russian], Abstract, XIII Vses. Shkoly po Morskoj Geol., Inst. Okean. Akad. Nauk SSSR, Moscow (1988).
19. F. V. Chukrov, L. E. Shterenberg, A. I. Gorshkov, et al., "Nature of the 10 Å manganese minerals in oceanic ferromanganese nodules," *Litol. Polezn. Iskop.*, No. 3, 33-41 (1983).
20. L. E. Shterenberg, G. A. Dubinina, and K. A. Stepanova, "The formation of flattened concretions," in: *Problems in the Lithology and Geochemistry of sedimentary Rocks and Ores* [in Russian], Nauka, Moscow (1975), pp. 166-181.
21. L. E. Shterenberg, A. I. Gorshkov, G. A. Dubinina, et al., "Formation of todorokite and birnessite in ferromanganese nodules in the Black Sea," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 7, pp. 94-98 (1985).
22. L. E. Shterenberg, V. A. Alexandrova, I. F. Gablina, et al., "Composition and structure of manganese crusts in the sea of Japan," *Tikhookean. Geol.*, No. 1, 125-128 (1986).
23. E. Bonatti, M. Zebri, R. Kay, and H. S. Rydell, "Metalliferous deposits from the Apennine ophiolites: Mesozoic equivalents of modern deposits from oceanic spreading centers," *Bull. Am. Geol. Soc.*, 87, 83-94 (1980).
24. E. V. Grill, R. L. Chase, R. D. MacDonald, and J. W. Murray, "A hydrothermal deposit from Explorer Ridge in the northeast Pacific Ocean," *Earth Planet. Sci. Lett.*, 52, No. 1, 142-150 (1981).
25. H. Harder, "Nontronite synthesis at low temperatures," *Chem. Geol.*, 18, pp. 169-180 (1979).
26. S. A. Moorby and D. S. Cronan, "The geochemistry of hydrothermal and pelagic sediments from the Galapagos Hydrothermal Mounds fields, DSDP Leg 70," *Miner. Mag.*, 47, No. 344, pp. 291-300 (1983).
27. S. A. Moorby, D. S. Cronan, and G. P. Glasby, "Geochemistry of hydrothermal Mn-oxide deposits from the S. W. Pacific island arc," *Geochim. Cosmochim. Acta*, 48, pp. 433-441 (1984).
28. E. L. Schrader, B. R. Rosendahl, W. J. Furbish, and D. P. Matthey, "Mineralogy and geochemistry of hydrothermal and pelagic sediments from the Mounds Hydrothermal Field, Galapagos spreading center: DSDP Leg 54," *J. Sed. Petrol.*, 50, No. 3, pp. 918-928 (1980).
29. M. D. Siegel and S. Turner, "Crystalline todorokite associated with biogenic debris in manganese nodules," *Science*, 219, No. 4581, pp. 172-174 (1983).
30. G. Thompson, M. J. Mottle, and P. A. Rona, "Morphology, mineralogy, and chemistry of hydrothermal deposits from the TAG area, 26° N, Mid-Atlantic Ridge," *Chem. Geol.*, 49, No. 1-3, 243-257 (1985).

The paper presents theories on the origins of Far Eastern phosphorites that formed in unstable tectonic settings. A proposed formation mechanism for the first time involves a new lithological category of phosphorites, associated with thixotropic deformational changes of phosphate deposits. Four basic phosphate categories were recognized. These, formed through postdepositional processes, are the vein-breccia; diapiric-dropstone; convoluted-microfolded; and "fragmented"-layered categories. The injected-convoluted category of redistributed phosphates never display orientation within the enclosing rocks. This led to depletion of primary-sedimentary phosphorite concentrates. If traditional assumptions are employed regarding their layered character, this may lead to major errors when mapping such deposits.

Phosphorites, that carry no indications of having been deposited in water and possessing characteristics of postdepositional origins, are widespread among ancient phosphorites in the Asian parts of the USSR and adjacent countries. One of the most obvious postdepositional phosphorite is of vein-brecciated character, described in the Lesser Khingan area [2, 12, 16], in the Udsk-Shantarsk phosphorite basin [13], in China [2], and outside the Far East region at several locations in the Altai-Sayan folded belt [4, 10], in the Aksu-Bailiustinsk Zone of N. Kazakhstan [1]. In spite of its superimposed character, the deposit often is associated with sedimentary processes [14, 17, 18], with subaqueous, wave dominated settings and seismic brecciation [9]. Other workers related these peculiar breccias to karst development [16], to subaerial soil zones [12], hydrothermal karst processes [13], metasomatic processes [4], and katagenetic alterations [10]. Heated discussions had also been conducted on the origins of other phosphorite varieties with unclear indications of underwater deposition. The injectional-convoluted type has not yet been included among the present lithological-genetic phosphorite classifications. Formations that may qualify for inclusion into this category are widespread.

Studies of Bureinsk Massif phosphorites, investigated by the author in 1979-1988, especially in the Lesser Khingan region (Fig. 1), the Yudom-Maisk Basin, also comparative studies on rock samples derived from the Udsk-Shantarsk phosphorite basin ("USHB") and presently located in the Roganov-Sobolev collection, provided data that conflicted with the previously listed genetic theories. Let us now review the basic aspects of postdepositional phosphorites in the Far East. All of them are characterized by so-called microspheritic, structureless phosphate, located in a given textural-structural interrelationship with the petrological background. The following rock categories have been identified.

Vein-breccia phosphorites are characterized by complex, coarsely lenticular, lenticular or irregular bodies, including columnar shapes, controlled by bedding planes, often with gradual transition into phosphate-free rocks. The boundaries toward these rocks can only be defined by means of sample analysis. Linear dimensions of these bodies range between a few tens of meters and several hundred meters. Narrowing of the rock bodies does occur laterally.

Phosphate precipitates in these rocks are represented by complex interweaving of veinlike inclusions of phosphatic, less often, carbonate-phosphate and siliceous-phosphate composition. Rare phosphate precipitates occur along the rock body margins in the form of irregular, small veins with bulges, oriented within the enclosing rocks with a frequency of 2-3 to 10-15/per 1 m distance (Fig. 2a). The veins range in thickness from fraction of a cm to several centimeters. Where they thicken and widen, the veins of the substrate rocks were destroyed as phosphate broke the veins into angular fragments. These fragments range from fractions of a

Far Eastern Scientific-Research Institute for Mineral Resources, Khabarovsk. Translated from *Litologiya i Poleznye Iskopaemye*, No. 4, pp. 41-53, July-August, 1989. Original article submitted May 30, 1988.

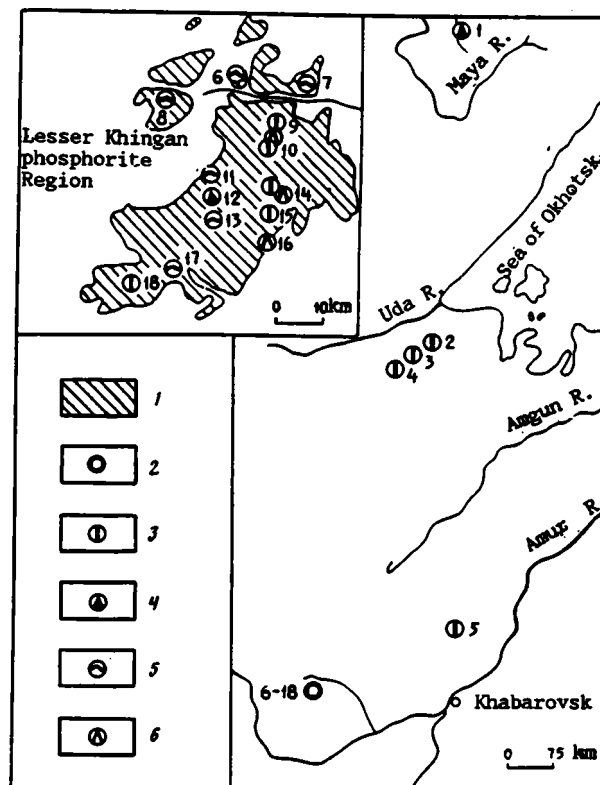


Fig. 1. Index map of injected-convoluted phosphorite deposits of the Far East: 1) phosphorite-bearing Riphean-Cambrian deposits the Lesser Khingan area (phosphorite occurrences and deposits); 2) not a specialized category; 3) vein-breccia type; 4) diapir-dropstone type; 5) convoluted-dislocated types; 6) "fragmented"-layered. Deposit and location names: 1) Gorbinsk; 2) Nel'kansk; 3) Nimisk; 4) Lagansk; 5) Sel'gonsk; 6) Birakans; 7) Londokovsk; 8) Kimkansk; 9) N. Murandavsk; 10) Burunbavsk; 11-13) Ditursk; 14) Novoditursk; 15) Tigrovaya Pad'; 16) Gremuchinsk; 17) Romashka; 18) Bidzhansk.

millimeter to tens of centimeters (Fig. 2b). Field studies have shown that the vein inclusions represent stockworks. Light-colored, massive dolomites and limestones represented the substrate for the vein system in the Lesser Khingan and Vandansk Ridge area, elsewhere while microquartzites (UShB area) did.

In areas where the vein matter predominates, the rock obtains a brecciated structure. In a number of instances these features became filled with fine, angular fragments of rounded (oncolitic?) dolomite grains, with the complete absence of large grains. Occasionally, fragments of the substrate were fringed by siliceous or carbonate margins. The P_2O_5 content in the vein-breccia formations ranged between fractions of one percent to 36.4% within a distance of 0.5 m, depending directly on the amount of phosphate cement and is directly dependant on the amount of phosphatic matter. Large part of this matter is in close association with the "fragments." The vein-breccia system quite often is associated lengthwise or in its roof with layers and lenticular bodies that range in size from 0.1-0.5 m to several meters. The bodies are oriented along the bedding plane and wedge out quickly. They are composed of gray, thin beds that alternate rhythmically, containing phosphate and phosphatic carbonate matter. Identifiable, individual phosphate layers are rare, as expressed by the tight intergrowth between phosphate and pelitic carbonate matter. Depositional-type phosphate breccias with phosphate fragments often are associated with vein-breccia phosphorites.

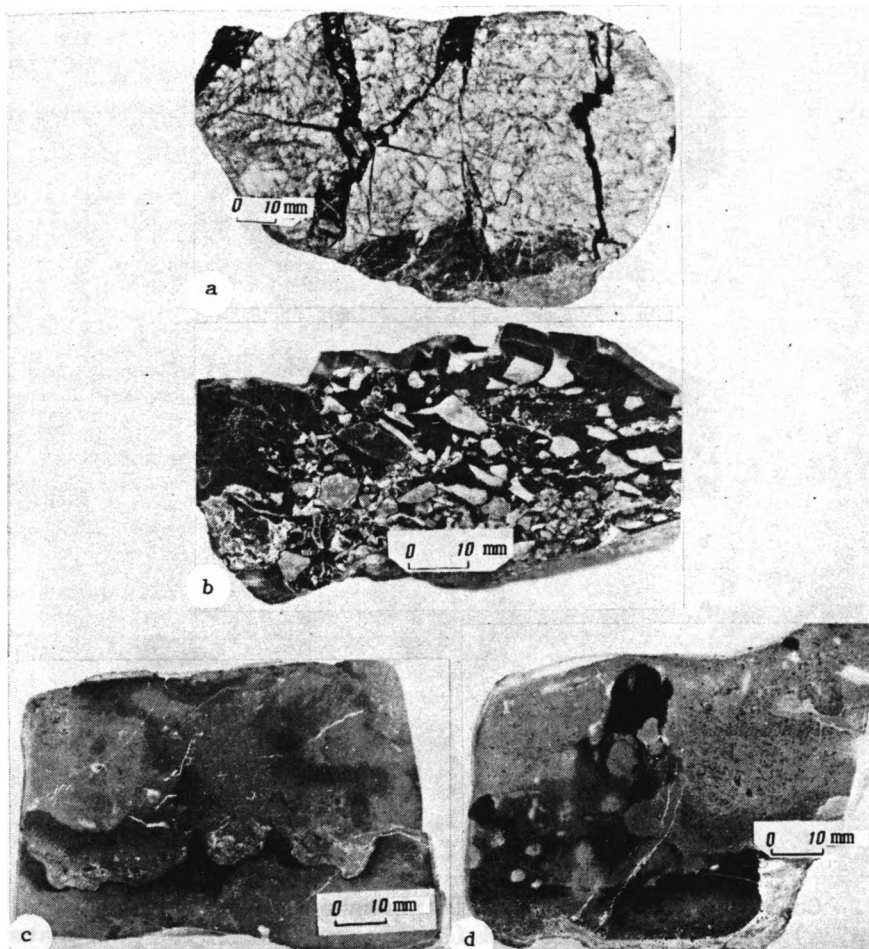


Fig. 2. Injected phosphate: a) vein (black; phosphate; gray: dolomite); b) brecciated (black: phosphate, gray and light gray: dolomite fragments; Burunbavsk location, Lesser Khingan region); c) diapir-type; d) dropstone-type (black: phosphate; dark-gray: phosphatic-limey matter, gray: limestone; Gorbinsk location, Yudom-Maisk Depression).

The phosphate matter of vein-breccias phosphorites is represented by microscopically homogenous, black matter, with various shades of pelitic substance, often crowded with fine, angular fragments of the substrate. In the thin veins the phosphate usually is "cleaner" and contains no mechanical admixtures. Large numbers of very fine, practically phosphate-free dendritic, limey black veinlets fringe the veins in a number of Lesser Khingan locations. Similar veinlets occur also in dolomite fragments, enclosed within phosphate cement. It is obvious in both instances that the veinlets penetrate the substrate rocks on the outside of the phosphatic vein matter, forming a zone of maximum impregnation at the contact with the vein phosphate matter. The organic carbon content in the impregnated zones and in the phosphorite amounted to 0.10-0.82%, or 1.77-15.67%, when calculated as the ratio of the carbonate-free rock fraction.

Under microscope, the phosphate is cinnamon brown or dirty gray. Fine quartz, isolated carbonate and pyrite grain inclusions occur in the homogeneous matter. The phosphate is poorly crystallized, almost isotropic. It displays clear anisotropy only in the contact zones with granitic intrusives. Contacts with the enclosed rocks are generally sharp and clearcut, although sinuous reaction rims in phosphate and carbonate are visible at great magnification. Microscopic carbonate inclusions that occur with direct contact within the phosphate, often have crystallographic contours and only rarely display irregular embayment borders that intrude the phosphate.

The interrelationship between phosphate inclusions and the enclosing rocks helps proving that the inclusions were superimposed on already lithified sediments. In particular, it is

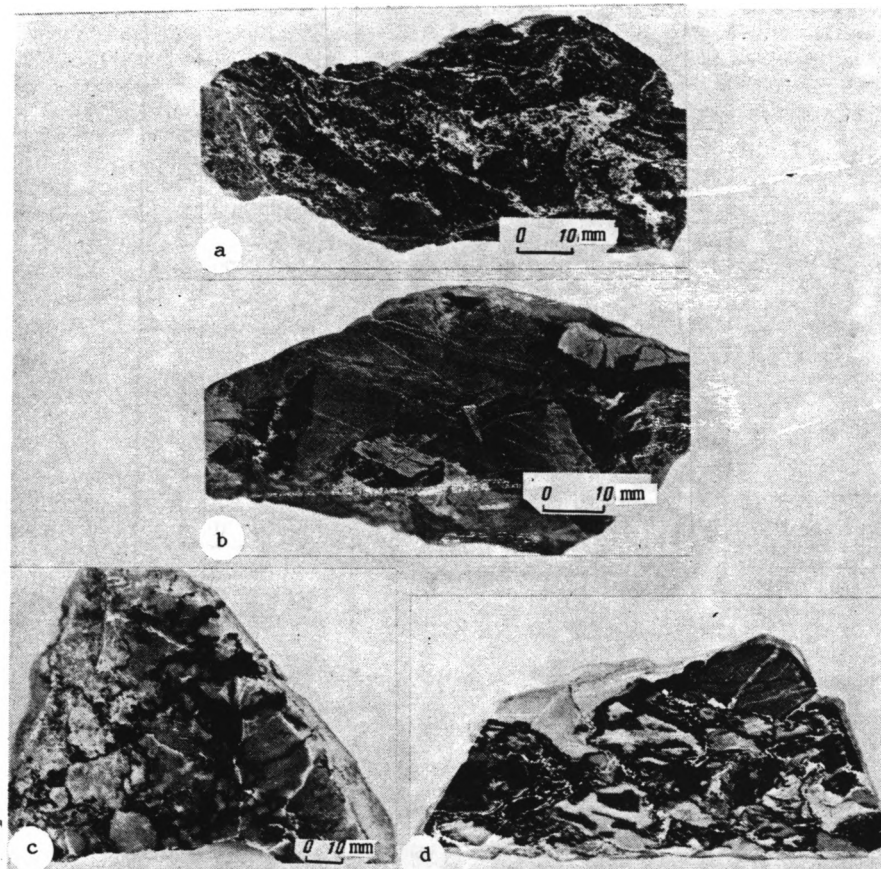


Fig. 3. Convoluted dislocations in phosphorites of the Lesser Khingan, a) horizontal microfold (dark gray and gray: phosphate; light gray: siliceous-clayey matter, Romashka locality); b) fractured layers and "cakes" of phosphatic (dark gray) and dolomitic (light gray) composition, Burunbavsk locality; c) convoluted pseudobreccias; d) lamellar "homogenized" pseudobreccias (black: phosphate; rest: limestone, Ditursk locality).

shown by their crosscutting character with relation to bedding plane. The process occurs especially through phosphatization along cleavage planes, fractures and sometimes through vein-separation of various structural units.

Diapiric-Dropstone Phosphorites. Phosphorite dropstone structures have been identified by the author in Lower Cambrian variegated formation of the Yudoma Basin. The phosphate mineralization occurs in the upper part of the formation as thin (0.5-2 cm) microphosphoritic layers, interlayered with greenish-gray glauconitic limestones (3-10 cm). The limestone beds display interference ripple mark-covered bedding planes; 1-2 cm high ripple crests with 5-8 cm spacing. Glauconite grains are widespread in the limestones, they mostly occur between ripple crests. Pyrite concretions also occur. Phosphatic rinds cover the uneven surface of the underlying limestones and may be followed across the entire (10-20 m) exposure area. The specially prepared slabs display such nodule like, glossy black crusts on the phosphate surface. Possibly, they are partly hardgrounds but in many instances carry structural features of postdepositional deformation. In transverse cuts they often display features of phosphate intrusion. These are distributed mostly over the ripple crests; thus increasing the crest height (Fig. 3a). The intrusion features form irregular vertical or inclined growths of maximum 3-5 cm. Sometimes they reach overlying bedding planes and even pierce them. The thickness of this phosphatic crust is unevenly reduced in the intercrest zones until it disappears completely. Individual layers are associated with dropstonelike inclusions of 5-15 mm. They occur a few cm above the lower phosphate layers. The lower layers typically are very thin (less than 1 cm) and are characterized by the "cloudy" (pseudodetrital) texture of the adjacent limestones. Simular pseudodetrital texture occurs between dropstone inclusions and underlying phosphate crusts (Fig. 2b) at very short distances.

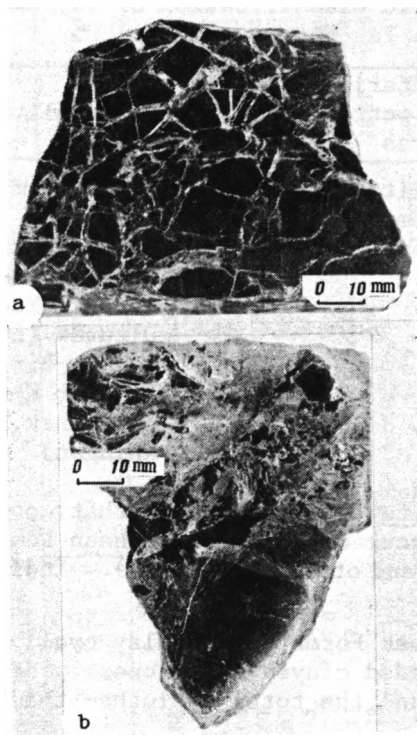


Fig. 4. "Fragmented"-layered phosphorites: a) breccia, formed by volume reduction in bedding plane (Gremuchinsk locality); b) breccia with phosphate fragments of various orientation (Burunbavsk locality) black: phosphate; gray: limey dolomite.

Diapiric and dropstone inclusions of the Lesser Khingan region occur in layers of convoluted-dislocated phosphate-carbonate rocks (Burunbaevsk and Ditursk localities).

Convoluted-Folded Phosphorites. Dislocated phosphate units within which the enclosed laminae have been disrupted. These form a complex microfold system in a number of Lesser Khingan outcrops (Ditursk, Birakansk, Kimkansk and Romashka). Independent of the intensity of the disruptions, no deformation occurred in the surface and upper portions of the beds. Several, 2-3-m-thick beds of intensively dislocated phosphate-carbonate rocks occur within the phosphate sequence in the Ditursk outcrop [8].

At other outcrops only individual parts of phosphate beds were affected by such dislocations. The deformation features are quite varied and are represented by complex dislocated undulating layers, miniature folds that are transitional toward a complex of diapiric, fan-shaped, or recumbent folds (Fig. 3a). Occasionally, the recumbent folds include "jet-shaped" features (Fig. 3b). Certain layers in the deformed interval, fraction of one cm thick and composed of microphosphoritic phosphate, preserved unbroken segments that can be traced to some distance. These are characterized by significant thickness changes, by thickening at the microfold hinges. The dimensions of individual elements in the microfolds are maximum 10 cm. In certain instances, the bedding planes acquire pseudodetrital, "scaly" structures, upward or downward transional (Fig. 3d) toward clearly detrital structures. The carbonate fragments in such structures have very irregular or rounded shapes, conformably adjusting to each other and often rimmed by cracked phosphate inclusions, among them individual fragments (Fig. 3c).

Microscopic studies indicated that despite the dislocations, phosphate inclusions proper, as in the vein-breccia phosphorites show significant differences in their individual appearance. The P_2O_5 content in such rocks ranges very broadly, between 1-20%.

TABLE 1. Lithological-Genetic Classification of Injected-Convolutated Thixotropic-Deformed Phosphorites of the Far East

Textural-structural types	Characteristics of basic petrological features	Localities and deposits
Vein-breccia-type	Quartzitic, dolomitic, limey	Lagansk; Nimisk, Nel'kansk (USHB), Sel'gonsk (Vandansk Ridge), Burunbaevsk, and other Pad', Ditursk (Lesser Khingan)
Diapir-dropstone-type	Limey	Gorbinsk (Yudom-Maisk Depression), Ditursk (Lesser Khingan)
Convolutated-folded	"	Ditursk, Birakansk, Romashka (Lesser Khingan)
"Fragmented"-layered	Limey, dolomitic	Gremuchinsk, Burunbavsk (Lesser Khingan)

"Fragmental"-Layered Phosphorites. Phosphorites that consist mostly of fragmental (decomposed) phosphorite laminae occur only in the Riphean Londokovsk Formation of the Lesser Khingan (Gremuchinsk, Burunbaevsk, and other localities). Individual phosphate bed outcrops also occur in many other locations.

The phosphates in the Londokovsk Formation display cyclic alternation of brecciated limey phosphorites and parallel-bedded clayey limestones. The thickness of the component cycles ranged from 0.1 m to 3-6 m and the total cyclothem thickness reached several tens of meters.

Phosphorite inclusions proper are represented by dense, black layer fragments of various orientation, ranging in thickness from fractions of one cm to 3-5 cm. In certain cycles the phosphorites retained layering but were broken into fragments that possessed polygonal outlines in horizontal projection. They were 3-5 cm in size, cut by a system of 5-8-mm-wide fractures. The fractures resemble desiccation cracks (Fig. 4a). Occasionally, a thin (15-20 cm) zone of transition develops from an undeformed layer, through a fractured interval with minor mixing of components, reaching to the phosphatic carbonate breccia. The fragments in these breccias were derived from broken phosphate layers that were then mixed. Crosscuts of the breccias are rectangular, sabre-shaped, occasionally curved in an arched fashion, irregularly deformed (Fig. 4b). The phosphate inclusions in these rocks are represented by microspheporitic, parallel-layered phosphorites. Their layering is represented by alternation of fine-grained carbonate and monophosphate or carbonate and phosphate-carbonate (occasionally siliceous-phosphatic) laminae. The layering is uneven, the thickness of the laminae range from 2 mm to 2 cm, rarely to 4-5 cm. The carbonate layers usually are thicker than the phosphate laminae.

Microscopic studies of the phosphate indicate that its extremely fine lamination is due to the very fine carbonate grain size.

Summary. The investigated phosphorites, while distinguished by a great variety of textural-structural features, have many common characteristics. Above all, they contain dark (carbon-bearing), very fine grained and cryptogranular (microspheporitic) matter with carbonate and quartz admixture. The microspheporitic phosphates [11] may have formed from marine phosphate-bearing mud-coagulate deposits. However, in basins, such as the Khubsugul, Yangtze and Florida Basins they have normal depositional parallel bedding, sometimes gradational layering. The absence of dislocation structures is typical of low-energy depositional conditions. The "clayey" phosphate's color was determined by the conditions of the medium. Black phosphate muds, in particular, are enriched in finely dispersed organic matter and accumulate in reducing environments.

Assuming that the Far Eastern microspheporitic phosphorites are essentially hardened muds, we have no indications of their direct deposition on the sea bottom. Apparently, their presence among the sediments was due to peculiar circumstances. It is very likely that the phosphate muds that accumulated in given zones, due to their state of dispersion and moisture content for an extended time period (under the protection of the overlying sediments, just as regular sediments do) acquired thixotropic character; a capacity for quick liquefaction and solidification under mechanical impact.

TABLE 2. Chemical Composition of Injected-Convolutated Phosphorites, Lesser Khingan

Phosphor- ite loca- tion No.*	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	CaO	MgO	K ₂ O	Na ₂ O	P ₂ O ₅	SO ₃	Calcin- ation loss	F	Σ	CO ₂	F/P ₂ O ₅
1	32,56	0,19	0,15	0,42	3,76	None	23,00	11,31	0,12	0,06	4,22	None	23,78	0,52	99,56	Not det.	0,123
2	8,05	0,11	0,23	0,31	0,22	"	40,54	10,04	0,16	0,03	16,36	"	21,72	1,25	99,02	"	0,076
3	6,33	0,07	0,36	0,40	0,25	Trace	39,98	11,67	0,36	0,36	13,02	0,14	26,72	0,32	99,78	24,5	0,026
4	5,95	None	0,60	0,20	None	None	51,85	2,50	0,04	0,06	9,60	None	28,80	0,51	99,60	Not det.	0,05
5	2,06	"	1,10	0,28	"	"	53,20	0,83	0,07	0,07	7,50	"	35,08	0,39	100,19	"	0,05
6	1,20	"	1,17	None	"	"	55,36	None	0,02	0,03	6,20	0,02	36,45	0,45	100,45	"	0,07
7	12,14	0,01	None	0,01	0,35	"	34,58	12,88	0,10	0,15	2,24	0,03	37,37	0,12	99,71	35,11	0,05
8	6,17	None	0,09	0,39	0,32	Trace	38,86	12,2	0,10	0,26	9,0	0,07	32,21	0,14	99,63	31,00	0,015
9	5,36	0,03	0,40	0,52	0,20	0,04	42,00	8,98	0,06	0,12	17,50	0,04	24,23	1,05	99,92	23,40	0,06
10	13,97	None	None	0,42	0,07	Trace	34,56	11,77	0,10	0,28	7,70	0,04	30,73	0,63	99,92	28,67	0,08

*1-3) Vein-breccia (Tigrovaya Pad' locality); 4-6) convoluted-dislocated type (Ditursk locality); 7-10) "fragmented"-layered type (Gremuchinsk locality). Analyses performed at Chemistry Laboratory, DVIMS.

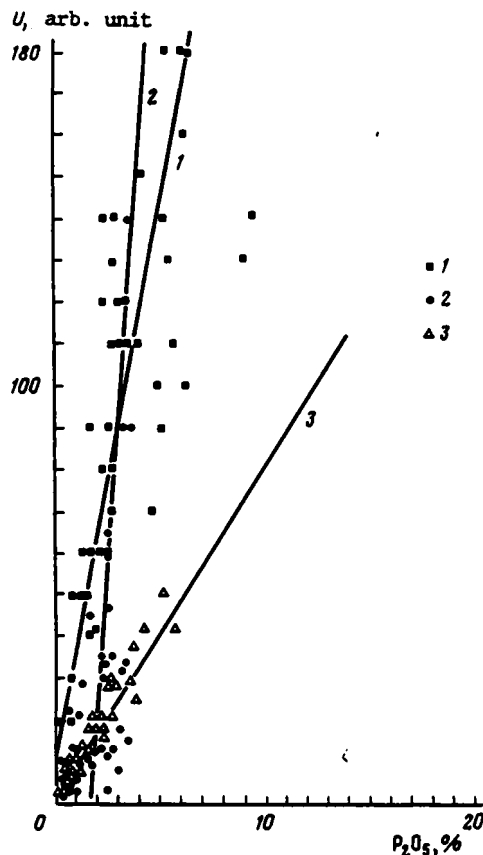


Fig. 5. U/P_2O_5 ratios in various phosphate rocks of the Lesser Khingan: 1) vein-breccia phosphorites, Tigrovaya Pad'; 2) convoluted-dislocated phosphorites, Ditursk; 3) "fragmented"-layered phosphorite type, Gremuchinsk.

Thixotropic changes in terrigenous deposits are widespread phenomena [3]. This is quite typical of deposition zones over steep marine slopes where the sediments are close to the critical balance and peculiar sediment discharge systems develop. Loosely packed deposits, composed of grains below 1 micron in diameter, may spontaneously liquify, but may also quickly harden. Optimum conditions for thixotropic changes occur in sediments with a 50-70% water content. Liquefied sediments with a quicksandlike consistency have reduced skeletal density ($1.14-1.58 \text{ g/cm}^3$), an increased porosity and moisture content, little or very low permeability to water and water-yield capacity. Under natural depositional conditions they have very low shear strength. Their natural angle of repose ranges between 3-9 degrees [7].

The quickly liquefied sediments undergo various deformations on the water bottom and while buried beneath overlying sediments, including consolidated deposits. In buried state, injectional and convoluted dislocations are widespread and lead to significant redistribution of the matter within the sediment beds. This renders them important agents of sediment transport.

At the moment of spontaneous liquification of the phosphate muds, due to certain mechanical impulses in the presence adequate pressure (e.g., in underwater slides; olistoliths during seismic events), the muds were probably injected into the enclosing rocks under overburden pressure. The muds filled the fracture system of already consolidated sediments or interbed space of the less hardened rocks. Apparently, this is how the vein-breccia phosphorites of the Lesser Khingan had formed. If injection phosphate systems do exist - what is the role of the primary depositional phosphate deposits in the process? How does one assign them? Detrital breccia, conglomerate-breccia, phosphate-gravel concentrates occur in a number of each of these systems. In these systems, phosphate is represented by dominantly angular fragments of different sizes, without sorting and orientation. Irregular blotches occur;

blobs of phosphates of poorly established identity. Apparently, the liquefied phosphate was squeezed into the adjacent fracture systems from these deposits. Originally, the phosphate muds also contained allotypic phosphate inclusions, called intraclasts by Riggs. They were in various stages of consolidation and lithification. The screening properties of the detrital components led to the squeezing out only of the liquefied mud fraction. The hard phosphate and carbonate inclusions could only be injected into the nearest and most open fractures. Most of them remained in the primary-depositional bodies. As the phosphate muds were hardening in fine, thread-shaped pores and microfractures within the fractures, they were dumped into the surrounding liquid medium that probably consisted of a water-bitumen suspension. This led to formation of dendritic, diffuse sediment bodies.

Calculations indicated that the linear dimensions of the stockwork, in comparison with the parent bodies, may increase by one order of magnitude, their volume by 2-3 orders of magnitude, with a corresponding decrease in the P_2O_5 concentration. At the same time, the primary-sedimentary bodies are reduced by 1.5-2-times. Because present deposits generally are 0.5-16 m thick, the expected width of the vein-breccia phosphate bodies may range between 5-160 m. This assumption agrees with field findings.

The formation of adsorptive-fracture complexes was independent of phosphate formation. Vein stockworks occur commonly around the periphery of ore bodies or without any interrelationship with them. They are filled with quartzitic or phosphate-quartz matter. Quartz, as a rule is pectinate, oriented perpendicular to the vein wall. This fact indicates that it precipitated in open fractures from muddy waters, that were squeezed out beyond the area of phosphorite-forming systems. So-called ornamented dolomites are very widespread in the immediate vicinity of the Lesser Khingan phosphate deposits. They were represented by dolomites, displaying vein-breccia structures with veins, with encrusted pectinate coarse-crystalline dolomites. The fracture systems with phosphate, quartz and dolomite formed during monotypic processes and differed only in the character of the mineral fill. The shape of the occurrences, certain "stratification" and simultaneous cross-cutting characteristics are typical of these deposits. The differences apparently relate to the fact that the first (phosphate and quartz-bearing) group was semiopen and associated with near-surface muds, including phosphatic muds; while the second group, was a closed system, not associated with muddy waters. The fractures probably formed initially during volume reduction due to dehydration of Mg- (Lesser Khingan area) and Si- metasomatism (UShB area) of the lime muds. This is shown by the very rare development of the discussed veinlets in the limestones, a more common development of these in dolomites and most common occurrence in quartzites.

Carbonate conglomerate-breccias, apparently of landslide origin have often been mapped in the immediate vicinity of the vein-breccia phosphorites, generally somewhat higher in the section. They are characterized by black limey micritic cement, in contrast with the light, dolomitic fragments, a strong predominance of cement, absence of fragment sorting and the presence of large individual detached blocks. Olistostrome formation are common in the top portion of phosphate deposits in the USHb-region [6].

In summary, it should be noted that the genetic questions of vein-breccia phosphorites often have been treated without a study of samples from poorly investigated phosphate deposits and in disregard to described examples of injected phosphorites, found in the literature. In certain instances [9, 13], the role of epigenetic alterations that supposedly lead to significant reworking of "primary" deposits, "smearing" of phosphate in the enclosing rocks, has been overestimated. Examples of such viewpoints that associate phosphates with weathering horizons, karst and hydrothermal karst reflect total disregard for the problems involved in the black coloration and carbon content of phosphates. Based on abundant information, it can be demonstrated that all epigenetic changes (including katagenetic, metamorphic, hydrothermal-metasomatic changes, karst and weathering crusts) lead to fractionation, self-purification or, conversely, to variegated coloration (in subaerial processes), higher crystallization degree of phosphates, features that are fairly easily recognized in given Far East phosphorite types. Katagenetic dissolution under pressure, in particular, results in phosphate recrystallization, with fluorite formation [15].

The genetic theory on the sedimentary-metasomatic vein-breccia phosphorites is considered more progressive. This takes into account the shape of the ore body that crosscuts layering. Actually, the replacement of carbonate inclusions in the cement by phosphate and the fracture walls may be assumed occasionally on the basis of their "digitate" reactive interrelationship. However, the metasomatic replacement of phosphate deposits along fracture systems, deeply penetrating basement rocks, may take place only due to changing chemistry of the solutions

that invariably leads to metasomatic zonation. Field observations indicated that the micro-sphoritic phosphates are practically identical in different parts of the deposits. This indicates that an already composed, uniform matter penetrates the fracture system, only imparting it with the liquid characteristics of the liquefied phosphate mud-coagulate.

Forced by pressure into the fractures, it obviously may interact with the matter in the fracture walls but these reactions, thanks to the thixotropic changes that cause fast sediment hardening, cease at correspondingly fast rates. Therefore, they may be only of limited importance.

The diapir-dropstone phosphates, discussed above are probably associated with thixotropic changes of the phosphate muds during spontaneous liquefaction along the entire interlayer surface area in subaerial systems. Under the impact of gravity, hydrostatic suspension, and hydrodynamic pressure, the phosphate muds may flow from one part of a layer into another. The pressure redistribution resulted in the penetration of liquid matter into sediment layers above or below, within areas of greatest permeability and relatively less pressure. As the result, uneven "appendages" of liquefied matter formed on ripple crests where the pressure from overlying layers was somewhat reduced. Due to its weakness, matter in the appendages in certain instances is torn from the parent bed but it does not reach the overlying bed. This is how dropstone structures form (Fig. 2d).

Spontaneous liquefaction of consolidated sediments under overburden renders all overlying deposits unstable and at slight slope angles slippage of the top rock layers takes place in relation to the underlying liquefied bed. This leads to the modification in the transfer route of the liquefied muds. The parallel-layered phosphate muds with carbonate sediment layers of different degrees of consolidation may be deformed in such a manner that material is thoroughly mixed in the phosphate-carbonate beds within certain intervals and forms even-lamellar pseudobreccias. Such "homogenized" phosphate-carbonate beds achieve a thickness of 2-3 m in the Ditursk locality (Fig. 3d). They are interlayered with beds of convoluted-folded phosphate-carbonate rocks of microsphoritic phosphorites (0.1-1.0 m) and white, massive dolomitic limestones (3.0-6.0 m), crosscut by phosphate veins.

In contrast with the discussed varieties, "fractured"-layered phosphorites of the Londokovsk Formation, associated with the liquefaction and transfer of phosphate muds in the enclosed consolidated sediments represent results of bed deformation with unstable density layering: the overlying hardened layer (in this case, phosphate bed) is brittle. At the moment of spontaneous liquefaction of the underlying beds, composed of clayey-carbonate muds, the upper layer loses its support and starts to disintegrate. In the beginning, due to reduced volume, the higher, hardened phosphate layers broken into polygonal fragments by a syn-eris-driven fracture system (Fig. 4a). The fragments gradually sink into the liquefied bottom and remain suspended in various positions in the hardening matter (Fig. 4b). The multiple presence of such breccia layers in the section reflect a normal sedimentary sequence in which the breccias are not of sedimentary origin.

The above-discussed phosphorite varieties (Table 1) are most common in old complexes of the Far East. The enumerated genetic concepts indicate a two-stage phosphorite development. Phosphates include chemical (biochemical?) concentrates and quite pure, finely dispersed phosphate buried muds that later were redistributed within sediments that exhibit varying degrees of consolidation. The distribution mechanism involved thixotropic properties of phosphate muds or enclosed limey-clayey muds. Due to their ability to undergo spontaneous liquefaction, the muds may preserve or restore their viscosity and suffer various types of deformation. The following sequence of mud consolidation has been established on the basis of various observed interrelationships: dolomitic → limey → phosphatic → clayey-limey muds.

The chemical composition (Table 2) of postdepositional phosphorites, related to strictly defined niches of primary sedimentation differs only in the components that define the composition of the enclosing rocks, represented by the three basic categories (limestones, dolomites, quartzites) or their combinations. The distribution of element-admixtures in phosphorites depends on the organic content and the degree of its oxidation. The U-content (Fig. 5) is very low in the relatively better oxidized phosphorites that, due to prolonged exposure on the sea floor, became hardened ("fractured"-layered phosphorites of the Londokovsk Formation). The higher U-content is typical of vein-breccia and convoluted-folded phosphorites that form from muds that are relatively rapidly covered by sediments and hardened under un-aerobic conditions. Based on available data on relative uranium distribution, its concentration values in Far East phosphorites were found near-identical; a fact utilized in geophysical

exploration of phosphorites. In general, this phosphorite group is characterized by higher Mo content, less frequently by higher Pb, Li, and Sn content. Yt and Sr display a close correlation with "fractured"-layered phosphorites; the vein-breccia phosphorites correlate with the Cu content, less frequently, with Pb. Consequently, geochemical data also indicate a lesser degree of oxidation (i.e., enclosed conditions) of the vein-breccia type, in comparison with the "fractured"-layered phosphorites.

In evaluating the role of phosphate redistribution in the enclosing rocks, one must note their lack of orientation that leads to a significant impoverishment of the ore concentrates, even to their total elimination.

Injected-convoluted phosphorites are related to zones of sediment accumulation, characterized by an unstable tectonic regime. Apparently, seismic vibrations directly initiated their formation by causing thixotropic transformation of the phosphate muds; their luquefaction that triggered slides. Paul' [9] was correct in relating certain properties of Gornii Shori phosphorites to earthquakes.

Phosphate muds and their injected-convoluted derivatives may form in basins of marginal tectonically active platform zones, peri- and intracratonic depressions, and oceanic uplifts. This contrasts with the granular, microgranular phosphorites of the largest, mostly important phosphorite basins, located in the more stable, platform massif regions. That last type includes microsporitic phosphorites and probably also their injected-convoluted derivatives, although generally these have limited importance. In these instances, the phosphorite-bearing sections become quite complex, branch out, and undergo other changes.

The accumulative, "primary" phosphate concentrates are generally stratified within the basins. Certain types of the injected-convoluted, convoluted-folded, "fractured"-layered and other phosphate categories are also stratified but this is not the case at all with the injected vein-breccia system. In this system, numerous "beds," so mapped in the Altai-Sayan region [4, 5], in the USHB area and in the Lesser Khingan by geological exploration surveys, may have been only the artifacts of schematic correlation between phosphate intervals.

LITERATURE CITED

1. V. S. Aladyshev, "Lithology of phosphorite-bearing deposits of the Aksu-Bailyustinsk Zone, northern Kazakhstan," *Litol. Polezn. Iskop.*, No. 2, 107-117 (1981).
2. G. I. Bushinskii, *Ancient Asian Phosphorites and Their Genesis* [in Russian], Nauka, Moscow (1966).
3. R. Gradzinskii, A. Kostetskaya, A. Radomskii, and R. Ungur, *Sedimentology* [in Russian], Nedra, Moscow (1980).
4. É. A. Eganov, *Formation and Distribution Problems of Bedded Phosphorites* [in Russian], Nauka, Novosibirsk (1974).
5. É. A. Eganov, *The Structure of Phosphorite-Bearing Sediment Complexes* [in Russian], Nauka, Novosibirsk (1983).
6. V. A. Zagorodnykh, "Mélange of the Lagansk phosphorite deposit," in: *Phosphates of Eastern Asia and Adjacent Seas* [in Russian], DVNTs, Academy of Sciences of the USSR, 120-124 (1984).
7. V. D. Lomtadze, *Engineering Geology, Engineering Geodynamics* [in Russian], Nedra, Leningrad (1977).
8. V. A. Nagornyi and G. V. Roganov, "New data on carbonate phosphorites and phosphate-carbonate rocks in the Pre-Amur region," in: *Phosphate-Bearing Formations of the Far East* [in Russian], DVNTs, Academy of Sciences of the USSR, Vladivostok (1984), pp. 74-89.
9. R. K. Paul', *Litol. Polezn. Iskop.*, No. 6, 61-70 (1982).
10. R. K. Paul', "Formation conditions of the Gornoshorsk phosphorites," in: *Phosphates of Eastern Asia and Adjacent Seas* [in Russian], DVNTs, Vladivostok (1984), pp. 94-104.
11. S. Riggs, "Petrology of Tertiary phosphorite systems in Florida," in: *Geology of Phosphorite Deposits* [Russian translation], Mir, Moscow (1983), pp. 35-84.
12. G. V. Roganov, F. S. Oksengorn, G. D. Kuz'min, and G. D. Gorbacheva, "Phosphorite content of the eastern ore district in the Lesser Khingan area," in: *Metallogenesis in the Pre-Amur Region* [in Russian], DVNTs, Vladivostok (1981), pp. 102-112.
13. G. V. Roganov, L. P. Sobolev, S. Ya. Mel'nik, and G. B. Baldanov, *Udsk-Shantarsk Phosphorite Basin* [in Russian], Nauka, Novosibirsk (1986).
14. Yu. R. Ruchkina and A. A. Arsen'ev, "Phosphorite composition and categories in the Udsk-Shantarsk region," in: *Composition of Phosphorites* [in Russian], Nauka, Novosibirsk (1977), pp. 36-38.

15. L. P. Sobolev, "Katagenetic reorganization of phosphorites in the UdsK-Shantarsk Basin," in: Phosphorite-Bearing Formations of the Far East [in Russian], DVNTs of the Academy of Sciences of the USSR (1984).
16. N. I. Tambovtsev, "The problem of phosphorite content in iron ore deposits of the Lesser Khingan," Inf. Sb. VSEGEI, No. 22 (1959).
17. B. N. Fomin and E. L. Shkol'nik, "The phosphorite content of ancient Lesser Khingan deposits," in: Phosphates of the Far East [in Russian], Vladivostok (1980), pp. 121-130.
18. Phosphorites and Apatites of Siberia [in Russian], Nauka, Novosibirsk (1980).

PHYSICAL-CHEMICAL SETTINGS OF URANYLVANADATE ORE FORMATION

I. G. Zhil'tsova, S. A. Perlina, and E. M. Shmariovich

UDC 553.495:553.21/24

In standard conditions the solubility product (SP) has been determined for synthesized tuyamunite ($10^{-51.56}$) and the Gibbs free energy of formation of $\text{Ca}(\text{UO}_2)_2 \cdot (\text{V}_2\text{O}_8)$. This study determined that this mineral is formed instead of carnotite at abnormally high calcium activity, typical for highly calcareous environments. The uranylvanadate solubility minimum corresponds to a pH of 5.5-8.5. In neutral and alkaline settings these minerals are much more stable than are uranylphosphates and uranylarsenates.

Uranylvanadate mechanization is represented mainly by carnotite $\text{K}_2(\text{UO}_2)_2(\text{V}_2\text{O}_8) \cdot 3\text{H}_2\text{O}$ and its calcium analogue tuyamunite $\text{Ca}(\text{UO}_2)_2(\text{V}_2\text{O}_8) \cdot 8\text{H}_2\text{O}$. In an earlier paper [4], we reported the solubility product $10^{-57.35}$ and Gibbs free energy -1270.2 kcal/mol (without crystallization water, -1100.1 kcal/mol) of synthetic carnotite formation and described the physical-chemical conditions under which the mineral is formed. The data suggested that the mineral can be deposited in natural alkaline waters carrying uranium and vanadium when they become acidulated and during neutralization of strongly acid solutions formed during oxidation of sulfide-bearing rocks (which, among other things, results in carnotite ore formation in carbonaceous schists). Besides carnotite, tuyamunite is a widespread mineral of the uranium-vanadium deposit oxidation zone, where it is found near the surface. It was first discovered and studied in 1912 by Nenadkevich at the Tuyamuyun deposit. The shows of this mineral at that deposit are associated with karst cavities limestones filled calcite, barite, quartz, and iron oxides [7]. It usually associates with carnotites, other uranylvanadates, and uranothallite, schroekingerite, and barite; often it is the end product of oxidation of a primary uranium mineral. Tuyamunite, as well as carnotite, is a leading ore mineral of micaceous deposits in carbonaceous schists, where it occurs in association with other uranylvanadates, uranylphosphates, precipitation goethites, barites, alunites, and vanadium oxides [6].

To study the solubility of uranyl minerals and establish their thermodynamic constants, one can take synthetic analogues rather than natural formations (which mostly occur in a thin intergrowth with other, sometimes uranium, minerals (Table 1)).

Synthesis of tuyamunite proved to be extremely difficult. It is characterized by certain specific features and has not been described previously in the literature. For this reason, it deserves a separate publication. The variety of the mineral, produced by using a specially designed method, was identified by x-ray investigation and chemical analysis as tuyamunite $\text{Ca}_{0.9}(\text{UO}_2)_2(\text{V}_2\text{O}_8)_{0.9} \cdot 13.8\text{H}_2\text{O}$, with a water content higher than the theoretical estimate. The solubility of the synthesized tuyamunite was the same as the earlier estimates for carnotite [1] and uranylphosphates [2]; we studied it in an acid range at two pH values (2.10 and 2.80) in HCl solutions prepared from hydrochloric acid of a high purity classification and by distillate at $s:l = 1:100$. The experiments were conducted with a thermostat at 25°C and periodic stirring. Specimens were sampled every 2-3 days and analyzed to determine

All-Union Scientific-Research Institute of Mineral Resources, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 4, pp. 54-60, July-August, 1989. Original article submitted May 17, 1988.

TABLE 1. Chemical Analysis of Tuyamunite

Components	Natural 134 TM*			Synthesized specimen 23		
	weight %	molecular abundance	molecular ratio	weight %	molecular abundance	molecular ratio
UO ₃	56.68	1970	2	43.26	1600	2
V ₂ O ₅	20.44	1120	1.13	12.80	700	0.87
K ₂ O	0.59	62	0.06	—	—	—
Na ₂ O	0.95	150	0.15	—	—	—
CaO	4.40	785	0.8	14.90	2660	0.90
H ₂ O ⁻	11.67	6480	6.6	19.90	11050	13.8
CO ₂	None	—	—	8.72	1980	—
Σ	—	—	—	99.58	—	—
Formula	Ca _{0.8} (UO ₃) ₂ (V ₂ O ₅) _{1.1} ·6.6H ₂ O			Ca _{0.8} (UO ₃) ₂ (V ₂ O ₅) _{0.9} ·13.8H ₂ O		

*Due to the small amount of material, the analysis determined only the main components.

TABLE 2. Analytic Data on Concentration of U, V, and Ca in Solution from Dissolved Synthesized Tyuyamunite (specimen 23) at T = 25°C, p = 1 atm

Time, days	pH	U		V		Ca	
		g/liter	-lgC _U , moles/kg H ₂ O	g/liter	-lgC _V , moles/kg H ₂ O	g/liter	-lgC _{Ca} , moles/kg H ₂ O
11	2.10	0.0359	2.82	0.079	2.81	0.0312	3.11
1	2.80	0.0168	4.16	0.0037	4.14	0.0014	4.46
		0.0170	4.15	0.0039	4.12	0.0015	4.43
3	2.82	0.0250	3.98	0.0050	4.01	0.0017	4.37
		0.0251	3.97	0.0049	4.02	0.0018	4.35
5	2.86	0.0347	3.84	0.0070	3.86	0.0027	4.17
		0.0350	3.83	0.0072	3.85	0.0027	4.17
7	3.85	0.0366	3.82	0.0075	3.83	0.0029	4.14
		0.0367	3.81	0.0077	3.82	0.0030	4.13
9	2.86	0.0367	3.81	0.0080	3.80	0.0030	4.13
		0.0369	3.81	0.0082	3.79	0.0031	4.11
11	2.85	0.0370	3.81	0.0082	3.79	0.0032	4.10
		0.0372	3.80	0.0080	3.80	0.0033	4.08

TABLE 3. Chemical Analysis of Tuyamunite* (after dissolution)

Components	Weight, %	Molecular abundance	Molecular ratios
UO ₃	58.70	2050	2
V ₂ O ₅	18.00	990	0.96
CaO	6.40	1140	1.11
H ₂ O [±]	16.21	9000	8.8
Σ	99.31	—	—

*Formula 1.1CaO·2UO₃·V₂O₅·8.8H₂O or Ca_{1.1}(UO₃)₂(V₂O₅)·8.8H₂O.

the principal components (U, V, and Ca). The uranium concentration was determined by a volumetric titanophosphate-vanadate method, which is applicable to concentration of > 0.01%; vanadium was determined by a colorimetric phosphorus-tungsten method with sensitivity of 0.005%. Calcium was measured by the atomic-absorption method on a single-beam Hitachi instrument operating on the basis of a diffractational monochromator, with analytic line of Ca = 1422.7 nm. The resulting analytic data were utilized to calculate the solubility product at the final pH of 2.85 based on two parallel measurements. These data and equilibrium values at the final pH of 2.10 are given in Table 2.

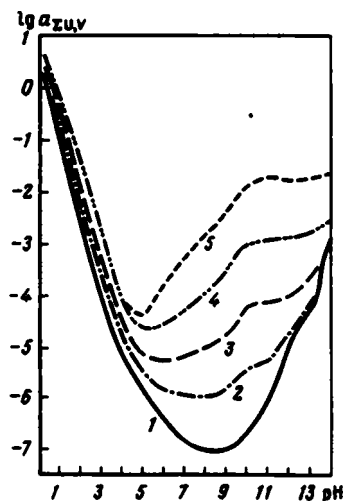


Fig. 1

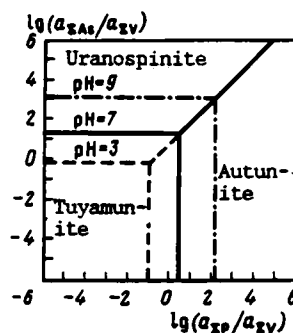


Fig. 2

Fig. 1. Calculation diagram of solubility (in mol/kg H₂O) of tuyamunite vs. pH: 1 - $a_{\Sigma\text{CO}_2} = a_{\Sigma\text{SO}_4} = 0$; 2 - $a_{\Sigma\text{CO}_2} = a_{\Sigma\text{SO}_4} = 0.001$; 3 - $a_{\Sigma\text{CO}_2} = a_{\Sigma\text{SO}_4} = 0.01$; 4 - $a_{\Sigma\text{CO}_2} = a_{\Sigma\text{SO}_4} = 0.1$; 5 - $a_{\Sigma\text{CO}_2} = 1.0$; $a_{\Sigma\text{SO}_4} = 0.1$ ($T = 25^\circ\text{C}$, $p = 1$ bar).

Fig. 2. Position of predominant fields of Ca-containing uranyl minerals: tuyamunite, autunite, and uranospinite as a function of the ratio of composite activities of phosphorus, arsenic, and vanadium in neutral (pH 7), acid (pH 3), and alkaline (pH 9) aqueous solutions ($T = 25^\circ\text{C}$, $p = 1$ bar).

Equilibrium was achieved on days 7-8, documented by a plateau on the curve. Solution evolved congruently, as indicated by x-ray investigation and chemical analysis, which confirmed that the solid phase after dissolution was tuyamunite $\text{Ca}_{1.1}(\text{UO}_2)_2(\text{V}_2\text{O}_8) \cdot 8.8\text{H}_2\text{O}$ (Table 3).

As in earlier publications, the activity coefficients γ_i for calculations of thermodynamic constants were determined from the Debye-Hückel formula [5], where a^0 for Ca^{2+} was 6.0.

The gross concentration of U in the water-salt system is determined by the sum of uranyl molalities, and its hydroxyl and Cl complexes:

$$C_{\Sigma\text{U}} = \frac{a_{\text{UO}_2^{2+}}}{\gamma_{\text{UO}_2^{2+}}} + \frac{a_{\text{UO}_2\text{Cl}^+}}{\gamma_{\text{UO}_2\text{Cl}^+}} + \frac{a_{(\text{UO}_2)_2(\text{OH})_2^{2+}}}{\gamma_{(\text{UO}_2)_2(\text{OH})_2^{2+}}} + a_{\text{UO}_2(\text{OH})_2^{2+}}; \quad (1)$$

calcium gross concentration is determined by the sum of molalities of calcium ions and its hydroxide complex:

$$C_{\Sigma\text{Ca}} = \frac{a_{\text{Ca}^{2+}}}{\gamma_{\text{Ca}^{2+}}} + \frac{a_{\text{CaOH}^+}}{\gamma_{\text{CaOH}^+}}; \quad (2)$$

the vanadium gross concentration is determined by the sum of molalities of orthovanadium acid and its dissociates:

$$C_{\Sigma\text{V}} = a_{\text{H}_2\text{VO}_4^{2+}} + \frac{a_{\text{H}_2\text{VO}_4^{2+}}}{\gamma_{\text{H}_2\text{VO}_4^{2+}}} + \frac{a_{\text{HVO}_4^{3-}}}{\gamma_{\text{HVO}_4^{3-}}} + \frac{a_{\text{VO}_4^{3-}}}{\gamma_{\text{VO}_4^{3-}}}. \quad (3)$$

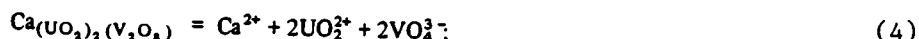
Tuyamunite solubility was studied in the acid region, and the three last terms of (1), the second term of (2), and the last two terms of (3) could thus be disregarded because of their smallness.

Calculations for the first series of tuyamunite dissolution tests, where $\text{pH}_{\text{in}} = 2.00$, $\text{pH}_{\text{fin}} = 2.10$, $\mu_{\text{calc}} = 0.01355$, $\log C_{\Sigma\text{U}} = -2.82$; $\log C_{\Sigma\text{Ca}} = -3.11$ and $\log C_{\Sigma\text{V}} = -2.81$ (we take for the average values $\log C_{\Sigma\text{U}} = \log C_{\Sigma\text{V}} = -2.81$), determined that: $\log \gamma_1 = 0.05$; $-\log \gamma'' = 0.19$; $\log a_{\text{UO}_2^{2+}} = -2.81 - 0.19 = -3.00$; $\log a_{\text{Ca}^{2+}} = -3.11 - 0.19 = -3.30$;

$$a_{\text{VO}_4^{3-}} = \frac{10^{-2.81}}{\frac{10^{-6.30}}{10^{-24.58}} + \frac{10^{-4.20}}{10^{-20.14}} + \frac{10^{-2.10}}{10^{-11.23}}} = 10^{-21.09};$$

$$\lg \Pi_{\text{Ca}(\text{UO}_2)_2(\text{V}_2\text{O}_8)} = \lg a_{\text{Ca}^{2+}} + 2 \lg a_{\text{UO}_2^{2+}} + 2 \lg a_{\text{VO}_4^{3-}} = -51.48$$

In the second series, at $\text{pH}_{\text{fin}} = 2.85$, the value was -51.65 . The average solubility product of tuyamunite was thus $10^{-51.56 \pm 0.09}$. The value of $\Delta G_f(298.15)$ of tuyamunite formation was estimated from the reaction equation



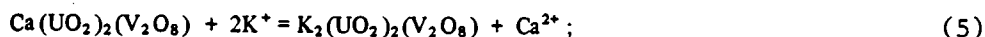
$$\Delta G_{\text{react}(1)} = (-1.364)(-51.56) = 70.33 \text{ kcal/mol}; \quad \Delta G_f \text{Ca}(\text{UO}_2)_2(\text{V}_2\text{O}_8) = -132.12 - 2.227.57 - 2.215.8 - 70.33 = 1089.19 \pm 0.12 \text{ kcal/mol}.$$

Figure 1 plots tuyamunite solubility vs. pH in a water medium devoid of sulfate and carbonate anions and containing them in various amounts (up to 0.1-1.0 mol/kg H_2O). The curve was plotted by using the same method as in earlier studies [2-4, 10].

Similar to its potassium analogue, studied previously, tuyamunite exhibited a minimal solubility in pure water in the pH range 6-10. In strongly carbonate solutions this minimum was shifted to a more acid region (pH 4.5-7.0). The solubility of the mineral for a given acidity level increased abruptly (at pH 8 $a_{\Sigma\text{CO}_2} = 1 \text{ mol/kg H}_2\text{O}$ by approximately a factor of 4.5 compared with a carbonate-free environment).

Generally, three regions of heightened tuyamunite solubility could be identified, as for other uranylvanadates: 1) acid (pH < 4.0-3.5), 2) alkaline (pH > 8.5-9.0), and 3) high-carbonaceous ($a_{\Sigma\text{CO}_2} > 0.01 \text{ mol/kg H}_2\text{O}$). Accordingly, by direct precipitation from the solution this mineral could be formed in three ways: 1) during neutralization of waters intensely acidulated as a result of oxidation of sulfide-bearing rocks or ores containing uranium and vanadium (the case of micaceous mineralization in carbonaceous schists [6, 10]); 2) in neutralization of alkaline waters containing U and V (possible mineralization variety in calcrites [11]); and 3) at degassing (decarbonitization) of rising fissure-vein carbon dioxide solutions which transported uranium and vanadium (the case of Tuyamuyun deposit [7]). The first genetic variety is typically associated with segregates of sulfate, iron oxides, and vanadium oxides; the second is possibly associated with isolates of silica, montmorillonite, and hydromica; the third is primarily characterized by a paragenesis with neomorphous calcite filling crack cavities and karst caverns [6].

The equilibrium between the leading natural uranylvanadates - tuyamunite and carnotite - is determined by the reaction equation



$$\log K (\text{reaction (2)}) = -8.04 + -1.364 = 5.89; \text{ whence, } \log a_{\text{Ca}^{2+}} + -2 \log a_{\text{K}^+} = 5.89.$$

We see that, if the ratio of Ca^{2+} activity to squared K^+ ion activity is greater than $10^{5.89}$, tuyamunite is formed; when the ratio is smaller carnotite is formed.

Table 4 gives averaged data on concentration in natural subsurface waters of various landscape and climate environments of calcium and potassium (based on data reported in [9]), and the ratios of Ca^{2+} activity and squared K^+ calculated with adjustment for the ionic strength of these aquatic solutions.

We see that in any landscape with subsurface waters with background Ca and K concentrations, carnotite is formed in terms of thermodynamics when the uranylvanadate solubility product reaches a certain level (rather than tuyamunite). Carnotite should therefore be viewed as the principal uranylvanadate mineral of oxidative hypergenesis. With all other conditions being equal, settings favoring precipitation of tuyamunite from subsurface water of average

TABLE 4. Ratios $a_{Ca^{2+}}/a_{K^+}^2$ Characterizing the Averaged Composition of Natural Subsurface Waters from Various Landscape and Climatic Zones of the Globe (based on data compiled by Shvartsev [9])

Quantity	Region					Global average
	trophic-subtropic	permafrost	temperate climate	mountains	continental salinization	
$-\lg C_{\Sigma Ca}$	3,38	3,28	3,03	3,13	2,54	2,96
$-\lg C_{\Sigma K}$	4,24	4,54	4,11	4,51	3,41	3,93
Ionic strength	0,0030	0,0028	0,0054	0,0039	0,027	0,0085
$-\lg \gamma'$	0,03	0,03	0,03	0,03	0,07	0,04
$-\lg \gamma''$	0,10	0,10	0,13	0,11	0,25	0,16
$-\lg a_{Ca^{2+}}$	3,48	3,38	3,16	3,24	2,79	3,12
$-\lg a_{K^+}$	4,27	4,57	4,14	4,54	3,48	3,97
$-\lg a_{Ca^{2+}} - 2 \lg a_{K^+}$	5,06	5,76	5,02	5,84	4,17	4,82

composition are typical for areas with permafrost ($a_{Ca^{2+}}/a_{K^+}^2 = 10^{5.67}$) and especially mountain regions, where the value of $a_{Ca^{2+}}/a_{K^+}^2$, equal to $10^{5.84}$ comes close to equilibrium of the two minerals ($10^{6.89}$).

Generally, tuyamunite formation instead of carnotite requires an additional source in water solutions, i.e., a surrounding lithologic environment rich in this component. According to Chernikov [8], deposits associated with limestones or sandstones containing considerable amounts of calcite are characterized by a predominance of tuyamunite over carnotite. This is observed, in particular, at Tuyamuyun deposit, in Todilto limestone deposits (Colorado Plateau, US), in vanadium-uranium oxidation zones in oil-bearing carbonate horizons in the intermontane depressions in the USSR, and in other locations.

The diagram in Fig. 2 shows the predominance of uranyl minerals containing the same Ca cation but belonging to different groups of uranium micas - tuyamunite, autunite, and uranospinite - depending on the ratio of gross concentrations in the solution of phosphorus, arsenic, and vanadium acids. These fields were calculated on the basis of thermodynamic constants [2, 3, 5]. We see that in a neutral environment (pH = 7) autunite is formed instead of tuyamunite if the phosphorus activity in water is higher than that of vanadium by a factor of 2.8. If arsenic is predominant over vanadium by a factor of 20.9, uranospinite is formed. In an acid medium (pH = 3), the tuyamunite field is sharply reduced. For its formation, vanadium activity must be as high as phosphorus by a factor of 11.2 and as that of arsenic by a factor of 1.6. In an alkaline setting, the opposite is the case: tuyamunite is formed instead of autunite and Ca-uranospinite already at $a_{\Sigma V}/a_{\Sigma P} > 0.0065$ and $a_{\Sigma V}/a_{\Sigma As} > 0.00054$. These data confirm our earlier [2, 6] conclusion on preferred formation of uranylvanadates in subneutral and moderate alkaline settings as opposed to uranylphosphates and most uranylarsenates, typical for moderately acid natural environments. The ratio of gross activity of arsenic and phosphoric acids above which Ca-uranospinite is formed instead of autunite is relatively stable and varies from 6.9 at a pH of 3 to 7.6 at a pH of 7, and 12.0 at a pH of 9. The data provide a foundation for quantitative interpretation of mineralogic and geochemical studies of oxidation zones of uranium ores containing vanadium, phosphorus, and arsenic and infiltrational ore accumulations of micaceous uranium mineralizations.

* * *

The following conclusions have been drawn from this study.

1. The experimental investigation helped determine the solubility product of synthesized uranylvanadate - tuyamunite - which fully corresponds in chemical composition and x-ray powder pattern to natural mineral (NM = $10^{-51.56 \pm 0.09}$). The calculated value $\Delta G_f(298.15)$ for this mineral, disregarding crystallization water, is -1089 ± 0.12 kcal/mol.

2. The solubility of tuyamunite, as well as of the uranylarsenates and uranylphosphates studied by us earlier, largely depends on the pH of the surrounding medium: it rises sharply in ultraacid and alkaline regions and is minimal in weakly acid and subneutral regions. A general rise of carbonate content is also conducive to transferring the mineral into a soluble state.

3. Ore uranylvanadate mineralization represented by carnotite and tuyamunite is mainly formed during acidulation of natural alkaline strongly acid waters and neutralization of these waters. Tuyamunite is formed instead of carnotite in an environment of a considerable excess of calcium ions over potassium ions at $a_{Ca^{2+}}/a_{K^{+}}^{2} > 10^{5.89}$). Tuyamunite formation is favored by more alkaline media than the settings for its phosphorous (autunite) and arsenic (uranospinite) analogues.

LITERATURE CITED

1. R. M. Garrels and C. L. Christ, Solutions, Minerals, Equilibrium [Russian translation], Mir, Moscow (1968).
2. I. G. Zhil'tsova, L. I. Polupanova, E. M. Shmariovich, and S. A. Perlina, "Physical and chemical conditions of formation of uranylphosphate mineralization," *Litol. Polezn. Iskop.*, No. 6, 71-82 (1985).
3. I. G. Zhil'tsova, L. I. Polupanova, E. M. Shmariovich, and S. A. Perlina, "Physical and chemical conditions of formation of uranylarsenate mineralization," *Litol. Polezn. Iskop.*, No. 8, 44-54 (1987).
4. I. G. Zhil'tsova, E. M. Shmariovich, L. I. Polupanova, and S. A. Perlina, "Physical and chemical conditions of formation of carnotite mineral ore," *Litol. Polezn. Iskop.*, No. 6, 49-60 (1982).
5. G. B. Naumov, B. N. Ryzhenko, and I. G. Khodakovskii, A Handbook of Thermodynamic Constant [in Russian], Atomizdat, Moscow (1971).
6. G. V. Pakul'nis, E. M. Shmariovich, I. G. Zhil'tsova, et al., "Mineral associations and physical-chemical formation conditions of micaceous uranium metallization in carbonaceous schists," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 1, 89-102 (1986).
7. N. N. Smol'yaninova, "Data on mineralogy and genesis of the Tuyamuyun deposit," in: *Essays on Geology and Geochemistry of Ore Deposits* [in Russian], Nauka, Moscow (1970), pp. 59-90.
8. A. A. Chernikov, Uranium Behavior in the Hypergenesis Zone [in Russian], Nedra, Moscow (1981).
9. S. L. Shvartsev, Hydrochemistry of the Hypergenesis Zone [in Russian], Nedra, Moscow (1981).
10. E. M. Shmariovich, I. G. Zhil'tsova, G. V. Pakul'nis, and G. A. Shugina, "The role of variations of environmental pH in formation of primary micaceous uranium metallization," *Sov. Geol.*, No. 2, 33-43 (1982).

AN ANALYSIS OF PATTERNS OF POST-SEDIMENTATIONAL FORMATION OF
PLIOCENE-QUATERNARY DEPOSITS OF THE BAKU ARCHIPELAGO
ON THE BASIS OF A FACTOR MODEL

A. S. Polyakov and B. A. Shmagin

UDC 552.13(479.24)

In the article, we discuss the results of a factor analysis carried out for a continuous section of Pliocene-Quaternary deposits of the Baku Archipelago. We analyzed 95 samples which were uniformly spaced with respect to depth (from 0.6 to 1255 m). Each of the samples was characterized by 31 variables characterizing the composition, structure, physical-chemical properties, and depth of occurrence of the deposits. As a result, patterns of post-sedimentational transformation of the deposits of the Baku Archipelago were discovered and quantitatively substantiated on the basis of facies characteristics. Evidence for phases of dia- and catagenesis is presented on the basis of the factor model obtained.

The study of patterns of post-sedimentational formation of deposits in modern water areas allows one to trace a continuous chain of processes associated with lithogenesis from the moment of sediment formation to its transformation into lithified rock. The necessity of such investigations is connected both with the development of a general theory of lithogenesis and with solutions to practical problems concerning rational use of the resources of the World Ocean. A great deal of data on the post-sedimentational formation, composition, structure, and physical-chemical properties of the deposits of the Caspian, Black, and Mediterranean Seas has been accumulated within the framework of investigations concerning the diagenesis and early catagenesis of marine deposits. Analysis of this material by traditional methods with the aid of paired dependences for variations in different characteristics with depth allowed us to mark off a series of steps in lithogenesis, grouped into stages of dia- and catagenesis [1, 3, 4]. It should be recognized, however, that what we have constructed does not cover the entire multiplicity of types of relationships between the samples studied.

The construction of a theoretical concept of the lithogenesis of marine deposits can only be carried out on the basis of a systematic approach to the sections being studied. Such an approach was realized in this research with the aid of one of the multivariate statistical methods (factor analysis), which we used to reveal and quantitatively characterize the patterns of post-sedimentational transformation of the Pliocene-Quaternary deposits of the Baku Archipelago. A continuous section of these deposits can be isolated as an independent system consisting of elements-samples, each of which is characterized by variables describing composition, structure, physical-mechanical properties, and thermobaric conditions. When investigating a given system, it is necessary to discover the structure of the relationships between characteristics of the deposits being studied, the variations in these relationships as a function of depth of occurrence of the sediments and rocks (reflecting thermobaric conditions), and also the manifestations of these relationships along the section.

Data for the investigations was in the form of 112 samples-monoliths selected at regular intervals of depth from four boreholes (holes 7, 9, 15, 16) drilled in the Baku Archipelago between the bank of Makarov and Los' Island (in the periclinal areas of the rises) and penetrating predominately clayey deposits of Pliocene-Quaternary age from the bottom surface (0.6 m) to a depth of 1255 m. Indices of composition, structure (structure and texture), and physical-mechanical properties were determined for the samples selected. The composition was characterized by the contents of CaCO_3 , C_{org} , and various clay minerals in the fraction smaller than 0.001 mm. The structure of the sediments was evaluated on the basis of grain-size composition and microtexture (the degree of orientation of the clay particles in the bedding plane). From among the physical-mechanical properties, we determined the moisture, specific

M. V. Lomonosov Moscow State University. Translated from *Litologiya i Poleznye Iskopaemye*, No. 4, pp. 61-73, July-August, 1989. Original article submitted January 29, 1987.

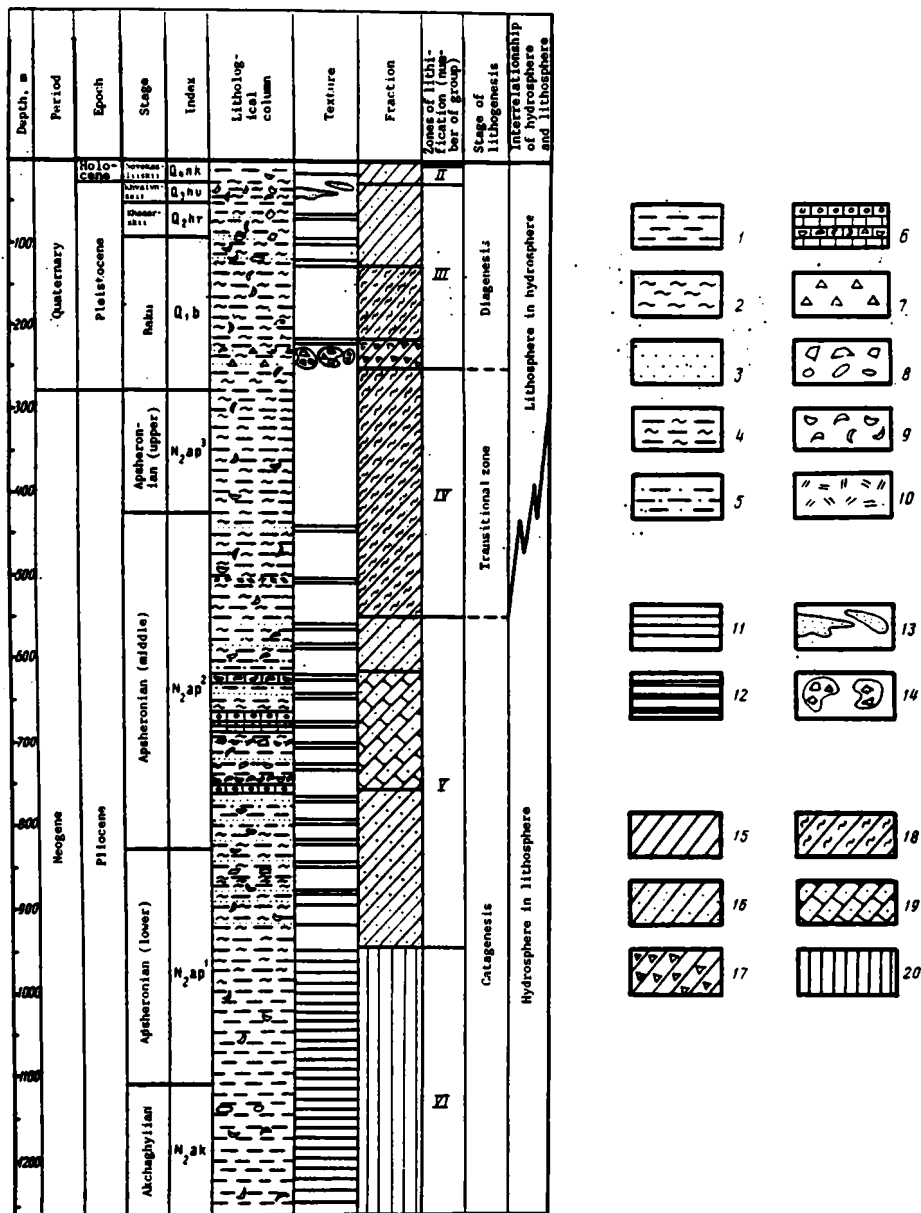


Fig. 1. Lithological-facies section of deposits of the Baku Archipelago and the patterns of their post-sedimentational transformation discovered. Lithological types: 1) Clay; 2) silts; 3) sands; 4) silty clay; 5) sandy clay; 6) limestone (oolitic, sandy, organic); 7) mud-volcanic breccia; 8) rock fragments, pebbles; 9) shells, detritus; 10) pyroclastic material. Textures: 11) Horizontal microlayering; 12) horizontal macrolayering; 13) lensiform; 14) brecciaform. Facies: 15) Clays and silty clay with shelly zones of placid sedimentation (lower regions of relief associated with the inner shelf); 16) silty and sandy clays with numerous interlayers of sand, shells and individual rock fragments and a pebbly zone of active bottom currents (slope of a bank or rises of the inner shelf); 17) silty clay of zone of active slope processes and mud volcanism (periclinal portion of a rise of the inner shelf); 18) silty clay with individual shells associated with a zone of relatively placid sedimentation (periclinal portion of the rise of the inner shelf); 19) silty and sandy clay with numerous interlayers of sands, shells, and oolitic, sandy, and organic limestones associated with the zone of active dynamics of the aqueous environment (foreshore portion of the bank of the inner shelf); 20) microlayers of clays with individual fragments of shells associated with a zone of placid sedimentation (depressions in the inner portion of the shelf).

TABLE 1. Results of a Factor-Regressive Analysis of a Model of Section.

No.	Variables	Index of variables	Mean	Standard deviation	Coeff. of variation	Smallest value
1	Depth from bottom, m	GLUB	432,25	421,04	0,97	0,65
2	Degree of orientation	ORIENT	0,51	0,28	0,54	0,22
3	Max. shear strength $\perp$ to bedding plane, kg/cm ³	TMAXV	5,77	7,31	1,27	0,28
4	Max. shear strength along bedding plane, kg/cm ³	TMAXHL	0,58	0,64	1,11	-0,7
5	Resistance to crushing, kg/cm ³	SIGM	5,15	9,49	1,84	0,73
6	Resistance to plastic deformation $\parallel$ to bedding, kg/cm ³	KONSH	22,48	22,19	0,99	0,05
7	Resistance to plastic deformation $\perp$ to bedding, kg/cm ³	KONSV	48,52	247,13	5,09	0,40
8	Anisotropy of shear strength	ANZTM	1,24	4,01	3,25	-16,50
9	0.01-0.005 mm fraction, %*	FR005L	1,23	0,25	0,21	0,43
10	Fraction <0.001 mm, %	FRM001	29,72	7,93	0,27	12,44
11	Fraction >0.05 mm, %	FRB05	2,74	5,26	1,92	0,0
12	0.05-0.001 mm fraction, %	FR1001	65,42	11,42	0,17	0,0
13	Fraction <0.01 mm, %	FRM01	78,38	19,91	0,25	53,7
14	Content of hydromica, %	GG	44,82	22,78	0,51	18,00
15	Content of mixed-layer minerals, %	GS	14,92	10,98	0,74	0,00
16	Content of kaolinite, %*	GKL	0,87	0,16	0,18	0,48
17	Content of CaCO ₃ , %*	CAC03L	1,1	0,17	0,15	0,83
18	Content of Corg, %*	CORGL	-0,24	0,23	-0,97	-0,82
19	Strength, %	PORST	0,37	0,09	0,25	0,14
20	Coefficient of porosity, %*	EL	-0,23	0,18	-0,78	-0,79
21	Natural moisture, %*	WEL	1,35	0,19	0,14	1,02
22	Yield point, %**	WFK	1925,72	599,11	0,31	900,00
23	Limit of plasticity, %	WP	23,46	5,10	0,22	16,5
24	Maximum molecular moisture capacity, %	WMMB	17,23	2,98	0,17	11,0
25	Hydroscopic moisture, %	WG	3,03	1,25	0,41	1,0
26	Flow index	PTEKL	-0,28	-0,21	-0,72	-0,68
27	Plasticity index	PPLASL	-0,03	0,22	-7,78	-0,44
28	Specific gravity of framework, g/cm ³	OBVES	-1,67	0,27	0,16	0,86
29	Plasticity number	MP	19,62	6,98	0,36	-15,30
30	Index of compaction	KUP	0,96	0,67	0,70	-0,92
31	Index of consistency	BS	0,04	0,67	16,11	-1,07
	Eigenvalues					
	Factors					
	Dispersion					
	Accumulated dispersion					

*Variable converted by taking logarithm.

**Variable converted by squaring.

Structural Relationships Between 31 Variables for the Entire

Greatest value	Coeff. of pair correlation with depth	Square of coefficient of multiple correlation (CMC)	Measure of sampling adequacy	Loads on factors									
				I	II	III	IV	V	VI	VII	VIII	IX	
1250,00	1,00	0,91	0,91	-0,85	0,32	-	-	-	-	-	-	-	
0,90	0,57	0,73	0,84	-0,66	-	-	-	-0,33	-0,27	-	-	-	
22,4	0,77	0,81	0,87	-0,67	0,34	-	-	-0,47	-	-	-	-	
1,31	-0,82	1,00	1,00	-0,67	0,43	-	-	-	0,28	-	-	-	
36,8	0,17	0,43	0,66	-0,27	-	-	-	0,76	-	-	-	-	
70,12	0,80	0,83	0,9	-0,79	0,31	-	-0,26	-	-	-	-	-	
72,75	0,00	0,13	0,45	-	-	-	-	-	-	-	-	0,82	
14,80	0,33	0,49	0,85	-	0,36	-	-	-0,53	-	-	-	-	
1,76	0,65	0,91	0,67	-0,49	0,56	-	-	-	-	-	-	-0,28	
53,85	0,15	0,88	0,44	-	0,40	0,31	-	-	-0,55	-	-	-	
29,15	-0,27	0,67	0,64	-	-0,79	-	-	-	-	-	-	-	
80,20	-0,13	0,78	0,39	-	-	-	0,89	-	-	-	-	-	
100,0	0,46	0,96	0,61	-0,31	0,57	0,26	0,49	-0,31	-	-	-	-	
71,00	0,24	0,53	0,57	-0,25	-	-	-	-	-	0,82	-	-	
46,00	-0,15	0,56	0,45	-	-	-	-	-	-	0,83	-0,35	-	
1,30	0,13	0,54	0,29	-	-	-	-	-	-	-	0,96	-	
1,49	-0,29	0,71	0,61	0,33	-	-	-	-	0,82	-	-	-	
0,58	-0,28	0,40	0,75	0,40	-	-	0,48	-	-	-	-	-	
0,68	-0,74	1,0	0,80	0,88	-	-	-	-	-	-	-	-	
0,32	-0,72	1,0	0,80	0,86	-	-	-	-	-	-	-	-	
1,95	-0,78	0,99	0,77	0,95	-	-	-	-	-	-	-	-	
3364,00	0,25	0,98	0,42	-	0,49	0,84	-	-	-	-	-	-	
35,00	0,39	0,94	0,47	-	0,72	-	-	-	-	-	-	-	
23,00	0,34	0,58	0,74	-	0,69	-	-	-	-	-	-	-	
9,89	0,33	0,46	0,72	-0,27	0,28	-	-	-0,28	0,31	-	-	-0,31	
0,18	-0,82	0,99	0,75	0,93	-	-0,25	-	-	-	-	-	-	
0,55	-0,84	1,00	1,00	0,94	-	-	-	-	-	-	-	-	
2,08	0,84	0,96	0,84	-0,93	-	-	-	-	-	-	-	-	
33,20	0,00	0,94	0,40	-	-	0,94	-	-	-	-	-	-	
2,07	0,73	1,00	1,00	-0,89	-	-	-	-	-	-	-	-	
1,92	-0,73	0,97	0,80	0,89	-	-	-	-	-	-	-	-	
				11,50	3,72	1,76	1,64	1,51	1,38	1,28	1,04	1,01	
				37,1	12,0	5,7	5,3	4,8	4,5	4,1	3,4	3,2	
				37,1	49,1	54,8	60,1	64,9	69,4	73,5	76,9	80,1	

gravity, density, porosity, limits of plasticity, various types of strength and a series of computational indices characterizing the dehydration and shrinkage of the rock. A composite lithological-facies section of the sediments investigated is presented in Fig. 1. One can familiarize oneself in more detail with the results of the lithological investigations using previously published reports [1, 3-5].

To solve the problems before us, we used probability (factor) modelling, including: 1) Framing the problems to be studied in the form of models of post-sedimental transformation of sediment; 2) schematization of the conditions associated with the post-sedimental transformation of the sediments and selection of variable characteristics associated with the conditions; 3) preparation of the original data in the form of a matrix $X(n \times p)$ (where n is the number of objects-samples and p is the number of variables used); 4) a statistical treatment of the original matrix block $X(n \times p)$ with the use of the procedure of factor analysis; 5) a discussion of the results within the framework of the problems posed and the factor models obtained.

As a starting model for the post-sedimental alteration of the Pliocene-Quaternary deposits of the Baku Archipelago, we used a model for the structure of the relationships between all of the characteristics (variables) of the sediments and rocks, including the depths of their occurrences, for the entire section as a whole. Schematization of the conditions associated with the post-sedimental formation of the deposits under consideration was carried out for 112 samples (objects) evenly distributed with respect to depth. For their characterization, 30 lithological indices of composition, structure, physical-mechanical properties, and the depths (from the surface) of occurrence were used, this amounted to 31 variables. After preliminary statistical processing of this body of data, several samples-objects insufficiently characterized by the variables were excluded from the analysis. The matrix of data for the starting model had an order $X(95 \times 31)$. In addition, distribution curves of individual variables over depth were normalized by taking logarithms or square roots of the original criteria.

Factor analysis in the R-modification with orthogonal (varimax) rotation of the factors [2] was applied to the matrix of the original data after standard statistical processing of the dependences obtained between the variables and depth. Interpretation of the results of the factor analysis was carried out on the basis of a matrix of factor loadings after varimax rotation of the factors to achieve a simple structure with the use of graphs of relative positions of the variables in factor planes. Diagrams of factor values were used to delineate groupings of objects-samples.

Results of the Investigations. I. Model of Structure of Relationships Between All Variables for the Section as a Whole. The factor analysis presents the structure of the correlation matrix for all variables (31) with respect to all (95) objects (samples). Let us consider the simplest pair correlation. The comparatively high values of pair correlations (Table 1) with depth of sample occurrence includes the following variables: logarithms of the indices of plasticity (-0.84) and flow (-0.82), specific gravity of the framework (0.84), shear strength measured along bedding (-0.82) and perpendicular to it (0.77), resistance to plastic deformation (0.80), the logarithm of the natural moisture (-0.78), the logarithm of the porosity coefficient (-0.72), porosity (-0.74) and also indices of compaction (0.73) and consistency (-0.73). The degree of orientation of clay particles (0.57) and the logarithm of the 0.01-0.005 mm fraction (0.65) have pair correlations at depths of more than 0.5 m. The remaining variables are characterized by significantly lower coefficients of pair correlation with depth. The square of the coefficient of multiple correlation (CMC) between the depth of occurrence of the samples and the remaining variables equals 0.91. The average value for the measure of sampling adequacy (0.77) indicates that the model is a good reflection of the variation associated with all the variables.

The structure of interrelationships between the variables is represented by nine factors (see Table 1) explaining 80.1% of the total dispersion of the variables. The natural moisture, indices of plasticity and flow, the index of consistency associated with them, and also porosity and the coefficient of porosity are included in Factor I (37.1% dispersion) with high positive loads; the specific gravity of the framework, the depths of occurrence of the samples, and the various indices of strength and degree of orientation of clay particles are included with high negative loads. This allows Factor I to be interpreted as a factor of dehydration and compression of the deposits with depth. Factor II (12.0% dispersion) loads the various granulometric fractions, the lower limit of plasticity, and the maximum molecular moisture capacity.

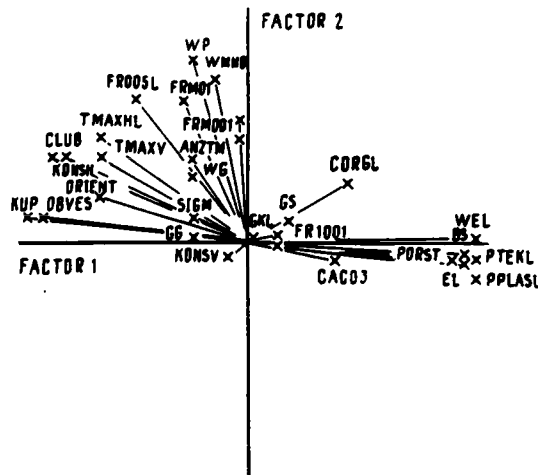


Fig. 2. Factor diagram of variables for complete model (for complete designations of the variables, see Table 2).

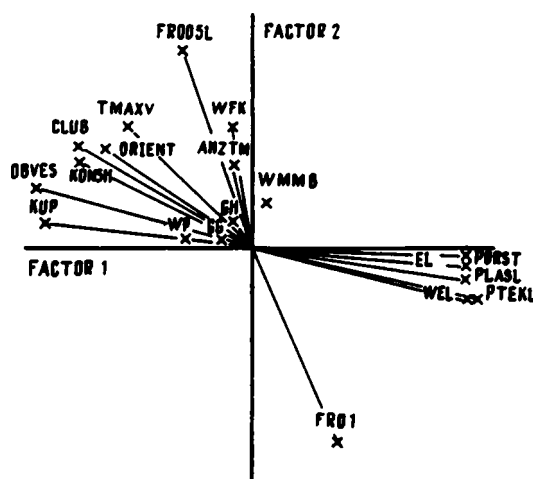


Fig. 3. Factor diagram of the variables in the condensed model (see Table 2 for a complete designations of variables).

Only one-two variables unconnected with the other variables are included in factors III-IX. Moreover, the eigenvalues of the factors, beginning with III, decrease sharply. Consequently, patterns of post-sedimentational transformation of the deposit under consideration, under conditions where they are buried to a depth of 1255 m, can be fairly completely characterized by the first two factors. Judging from the relative positions of the vectors associated with variables in the plane of factors I and II (Fig. 2), the variables characterizing the physical-mechanical properties of the rocks are the most sensitive to thermobaric variations, i.e., to variations in the depth of occurrence of deposits. As is evident from Fig. 2, vectors of resistance to plastic deformation, shear strength, degree of orientation of clay particles, specific gravity, and coefficient of compaction are aligned with the depth vector located in the negative region of Factor I. The vectors for natural moisture, the coefficient of porosity, and plasticity index are opposite in direction and have a good correlation with one another. Vectors for the lower limit of plasticity, maximum molecular moisture capacity, and the content of fractions < 0.001 and > 0.05 mm are positioned almost orthogonally to these groups. The vectors for anisotropy of strength and fractions 0.01-0.005 and < 0.01 mm are positioned near the vectors for shear strength. The vectors for contents of C_{org} and $CaCO_3$ gravitate toward the vectors for shear strength. The remaining variables are concentrated in the region of intersection of the axes associated with the factors under consideration. Thus, an analysis of the original model allowed us to discover the variables

TABLE 2. Results of a Factor-Regressive Analysis of a Model of the Structural Relationships Between 19 Variables for the Entire Section

No.	Variables	Index of variables	Mean	Standard deviation	Coefficients of variation	Smallest values	Largest values	Coeff. of pair correlation with depth	Square of coefficient of multiple correlation, CMC	Measure of sampling adequacy	Loads on factors			
											I	II	III	IV
1	Depth from bottom, m	GLUB	442,86	423,18	0,96	0,65	1250,00	1,00	0,91	0,88	-0,76	0,46	0,26	-
2	Degree of orientation	ORIENT	0,52	0,27	0,52	-1,92	0,90	0,57	0,63	0,94	-0,63	0,42	-	-
3	Max. shear strength $\perp$ to bedding plane, kg/cm ²	TMAXV	6,0	7,41	1,23	0,28	22,40	0,77	0,76	0,92	-0,55	0,52	0,32	-
4	Max. Shear strength along bedding plane, kg/cm ²	KONSH	22,94	22,05	0,96	0,05	70,12	0,78	0,77	0,95	-0,74	0,30	0,29	-
5	Anisotropy of shear strength	ANZTM	1,40	4,06	2,90	-16,50	14,80	0,35	0,53	0,78	0,47	0,44	-	-
6	0.01-0.005 mm fraction, %*	FR005L	1,24	0,24	0,20	0,78	1,76	0,66	0,80	0,81	-0,29	0,87	-	-
7	0.05-0.001 mm fraction %	FR01	16,69	13,21	0,79	0,00	41,51	-0,70	0,85	0,83	0,34	-0,81	-0,29	-
8	Content of hydromica	GG	44,92	22,98	0,51	18,00	71,00	0,25	0,85	0,53	-	-	-	0,93
9	Content of chlorite	GH	7,47	4,08	0,55	5,00	15,00	0,16	0,86	0,52	-	-	-	0,95
10	Porosity, %	PORST	0,37	0,10	0,26	0,14	0,68	-0,74	1,00	0,80	0,90	-	-	-
11	Coefficient of porosity*	EL	-0,23	0,18	-0,80	-0,79	0,32	-0,72	1,00	0,80	0,88	-	-	-
12	Natural moisture, %*	WEL	1,34	0,19	0,14	1,02	1,95	-0,79	1,00	0,79	0,93	-	-	-
13	Limit of flow, %**	WFK	1976,15	538,17	0,27	207,36	3364,00	0,27	0,95	0,38	-	-	0,79	-
14	Limit of plasticity, %	WP	23,96	3,87	0,16	16,50	35,00	0,42	0,99	0,47	-0,32	-	0,78	-
15	Max. molecular moisture capacity, %	WMMB	17,29	3,03	0,18	11,00	23,00	0,36	0,45	0,95	-	0,34	0,67	-
16	Flow index	PTEKL	-0,29	0,20	-0,69	-0,68	0,18	-0,83	0,99	0,80	0,88	-	-	-
17	Index of plasticity	PPLASL	-0,03	0,22	-0,15	-0,44	0,55	-0,83	0,99	0,78	0,92	-	-	-
18	Specific gravity of framework, g/cm ³	OBVES	1,67	0,27	0,16	0,86	2,08	0,84	0,97	0,86	-0,94	-	-	-
19	Index of compaction	KUP	1,00	0,65	0,65	-0,92	2,07	0,76	0,97	0,81	-0,92	-	-	-
	Eigenvalues										9,96	2,23	1,77	1,13
	Factors													
	Dispersion										52,4	11,8	9,3	5,9
	Cumulative dispersion										52,4	64,2	73,5	79,4

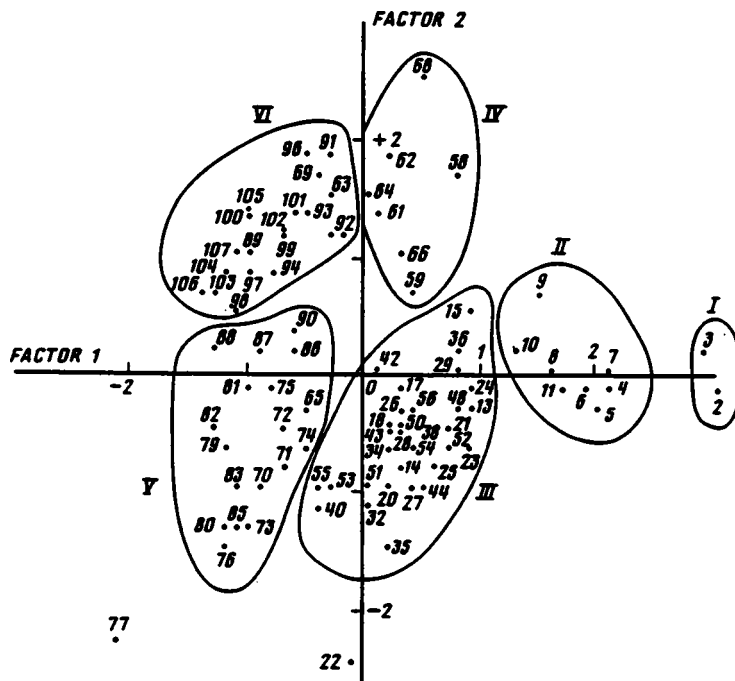


Fig. 4. Diagram of the distribution of samples in the plane of the first and second factors. Arabic numerals) sequential numeration of samples from the bottom surface to a depth of 1255 m; Roman numerals) numeration of individual groups of samples.

showing the strongest connection to the thermobaric conditions. In turn, this discovery made it possible to compose a model for the structure of relationships between variables most clearly reflecting the post-sedimentational formation of the deposits under consideration.

2. Model of the Structure of Relationships Between Variables Most Connected with Thermobaric Conditions. We included 18 variables and the depth of occurrence of objects-samples in the model (Table 2). The following variables possessed the highest pair correlations with depth the specific gravity of the framework (0.84), the logarithms of the indices of plasticity (-0.83) and flow (-0.83), the logarithm of natural moisture (-0.79), the index of compaction (0.76), porosity (-0.74), the logarithm of the coefficient of porosity (-0.72), the resistance to plastic deformation (0.78), the shear strength (0.77), the 0.05-0.01 mm fraction (-0.70), the logarithm of the 0.01-0.005 mm fraction (0.66), and the degree of orientation (0.57). The remaining variables possess significantly smaller coefficients of pair correlation with depth. The CMC (coefficient of multiple correlation) between depth of occurrence of samples and other variables amounted to 0.91. The mean value of the measure of sampling adequacy was 0.80, higher than in the preceding model.

Factor analysis of the model under consideration allowed us to uncover the structure inherent in the relationships between 19 of the variables under consideration and to represent their variation by means of four factors encompassing 79.4% of the total dispersion of the variables. The same variables were included in Factor II (52.4% dispersion) with high positive and negative loads that were included in the first model. The logarithms of the 0.01-0.005 mm fraction (0.87) and the 0.05-0.01 mm fraction (-0.81) were included in Factor II (11.8% dispersion). Consequently, factors I and II can be interpreted in the same way as in the preceding model.

The limit of flow, limit of plasticity, and maximum molecular moisture content were included in Factor III (9.3% dispersion) with high loads (0.79, 0.78, and 0.67 respectively). It is difficult to interpret this factor, since the variables entering into it depend in a very complex fashion upon the degree of dispersion and composition of the deposits. In addition, indices of flow, plasticity, consistency, and compaction (variables entering into Factor I) were calculated on the basis of the limits of flow and plasticity. Finally, only the content of chlorite (0.95) and hydromica (0.93) entered into Factor IV (5.9%), interpreted as

a factor associated with the mineral composition of the clay fraction. It should be excluded from further analysis of the model, since the two variables entering into it have no connection with the remaining variables.

The depth of occurrence of the samples significantly loads Factor I. The arrangement of vector-variables in the plane of factors I and II in the model under consideration (Fig. 3) is analogous to the distribution in the first model (see Fig. 2). It suggests that the condensed model preserves the structure of relationships between variables revealed in the first model. The relative positions of the vectors characterizing the dehydration, compaction, and strength of the rocks are also preserved in the plane of factors I and III. Only vectors characterizing the degree of dispersion of the rock, located along the plane of Factor I (which these vectors enter into with larger loads than in the case of Factor III) change their arrangement.

In accordance with the structural connections between the variables, six groups of objects-samples can be distinguished in the plane of factors I and II (Fig. 4). Two samples lying at depths as low as 5 m from the surface are included in the first group ($n = 2$). The second group ($n = 8$) consists of samples taken from the interval of 5-22 m. Samples found at depths of 22-250, 250-550, 550-928, and 928-1255 m make up the third ($n = 30$), fourth ($n = 9$), fifth ($n = 18$), and sixth ($n = 18$) groups respectively.

In the plane of factors I and III, only four groups of objects-samples can be distinguished. The first and second groups remain here as they were before, while the previous third-fourth groups and the fifth-six groups (isolated in factor planes I and II) are united into new third and fourth groups respectively.

Discussion of the Results. The factor model reflects the structure of relationships between the variables, which, in turn, reveals the nonhomogeneity of the section under investigation. The structure of relationships between variables which we obtained indicates that the variables characterizing the microtexture and physical-mechanical properties of the deposits under consideration are a reflection of the thermobaric conditions accompanying lithogenesis, conditions determined by burial of the sediments to depths to depths of 1255 m. Consequently, it is precisely these variables which can be used as quantitative criteria with respect to the post-sedimental transformation of marine sediments. The variables in the original model, characterizing the composition of the rock, did not enter into this group of variables and did not reflect processes of lithogenesis, probably because only the total content of one of another component of the sediment was taken into account and because the degree of transformation of this component was neglected.

On the basis of the structural connections between the variables (Fig. 3), the objects-samples were consolidated into six groups, each of which corresponded to an actual interval of the section. The positions of these intervals relative to the vectors of the variables and the factor axes show a number of quantitative patterns reflecting the post-sedimental transformation of the Pliocene-Quaternary deposits of the Baku Archipelago. The overall pattern is a sequential arrangement of intervals (from topmost I to the lowermost IV) along a depth vector which is aligned in a plane of Factor I, interpreted as a factor of dehydration, compaction, and strength of the deposits under consideration) (see Figs. 2 and 3). This provides a basis for interpreting the delineated intervals within the section as zones of lithification. The identical internal arrangement for intervals III-IV and V-VI with respect to a plane of Factor I and the separation of these intervals along Factor II (interpreted as a factor of dispersion) could be due to the influence of facies conditions associated with sediment accumulation during the processes of lithogenesis. This suggestion is also supported by the unification of these four intervals into two larger intervals in the plane of factors I and III. The fact that intervals of the section to a depth of 550 m (I-VI) are situated in the positive region of Factor I while the intervals associated with the lower portion of the section (V-VI) are situated in the negative region of this same factor deserves attention also. Since the vectors for the variables of moisture and porosity and the indices of flow and plasticity are aligned with the positive region of Factor I while the vectors for the variables of strength, specific gravity of the grit, and the degree of orientation of clay particles are aligned with the negative region of this factor, the transformation of the sediments down to a depth of 550 m should, in general, be connected with their dewatering, a decrease in porosity, and a change in consistency, while the post-sedimental alteration of the rocks lying below this depth should, in general, be connected with an intensification of the orientation of clay particles in the bedding plane and a formation of rigid structural bonds resulting in an increase in strength and anisotropy of strength of the deposits.

We will give a brief characterization of the composition, structure, and properties of the deposits along the intervals in order to confirm the patterns of post-sedimental transformation of the deposits under consideration as revealed by factor analysis.

The sediments of the topmost interval (I) are distinguished by maximum moisture (up to 89%) and porosity (up to 65%) and by minimum specific gravity of the framework (0.85 g/cm^3) and strength (0.09 kg/cm^2). The content of the fraction $< 0.01 \text{ mm}$ amounts to 75-80%, that of CaCO_3 equals 15-20%, and that of C_{org} equals 0.60-1.00%. A peculiarity of the sediments of this interval is the spontaneous dewatering and dehydration (syneresis) resulting from processes taking place in the benthic deposits.

The next interval (II) corresponds to sediments existing in a fluent state. The lower boundary of this interval ($\sim 22 \text{ m}$) coincides with a transition of deposits from a fluent state to a plastic state. The natural humidity, porosity, specific gravity of the framework, and strength respectively vary within the limits of this interval as follows: from 66 to 38%, from 65 to 49%, from 0.85 to 1.34 g/cm^3 , and from 0.09 to 0.50 kg/cm^2 . The average content of the pelitic fraction equals 76% and the quantities of CaCO_3 and C_{org} varying within ranges of 7-30 and 0.7-2.3% respectively.

Beginning with the next interval (III), the intensity of dehydration and compaction of the sediments gradually lessens. From the upper boundary of the interval ($\sim 22 \text{ m}$) to the lower boundary ($\sim 250 \text{ m}$), the indices of physical-mechanical properties vary in the following fashion: natural moisture, 38-25%; porosity, 49-38%; specific gravity of framework; 1.34 - 1.70 g/cm^3 ; strength, 0.5 - 3.0 kg/cm^2 . The deposits of the interval under consideration are more coarse-grained (average content of the fraction $< 0.01 \text{ mm}$ is 67%) and less limey ($\sim 10\% \text{ CaCO}_3$), and possess a smaller C_{org} content. The lower boundary of the interval corresponds to the transition to deposits in a plastic state to a solid one.

The rocks of interval IV exist in a solid state. Their natural moisture is less than the moisture of the plasticity boundary; this indicates the presence of primarily absorption-bonded water and a small quantity of free and "osmotic" water. A characteristic of these rocks is the formation within them of microtextures oriented in the bedding plane. The degree of orientation of clay particles in the first three intervals of a section equals approximately 0.5 (which corresponds to a random microtexture), and the average value for a given interval equals 0.72 (which suggests a predominant orientation of the particles in the bedding plane). The transition of the sediments to a solid state is also connected with the formation of more rigid, point-contacts between the particles. As a result, the strength of the rock increases sharply (up to 35 kg/cm^2 ; the average for the interval is 11 kg/cm^2); anisotropy of strength begins to appear; but breakage of the samples displays a brittle character. The processes of dehydration and compaction are weakly expressed. Within the interval, the natural moisture varies from 25 to 17%, the porosity varies from 38 to 30%, and the specific gravity of the framework varies from 1.70 to 1.90 g/cm^3 . The contents of CaCO_3 and C_{org} in the rocks remain approximately the same as in interval III; however, the quantity of fragments with pelitic dimensions ($< 0.01 \text{ mm}$) increases to 96%.

The deposits of interval V are characterized by the following lithological indices. The contents of CaCO_3 and C_{org} equal 7-15 and 0.27-53% respectively. The average content of the pelitic fraction equals 72%. The average value for the degree of orientation equals 0.57. The moisture, porosity, and specific gravity of the framework respectively vary with depth in the following fashions: from 15 to 13%; from 30 to 25%; from 1.9 to 2.0 g/cm^3 . The average strength for the entire interval equals 18 kg/cm^2 .

The rocks of interval VI are similar to the rocks of interval V with respect to composition and physical-mechanical properties. The difference consists only in the elevated content of particles smaller than 0.01 mm (an average of 99%) and a higher value for the degree of orientation of the clay particles (an average of 0.75).

The lithological data presented indicates that the delineated intervals of the section group together deposits with an identical degree of dehydration and correspondingly identical consistencies, porosities, specific gravities and strengths. Moreover, it is evident from these data that the intervals are differentiated also on the basis of the facies characteristic of the section, characteristics which manifest most clearly according to the degree of burial of the deposits (see Fig. 1).

Thus, factor analysis allowed us to reveal and quantitatively substantiate post-sedimental patterns of dehydration and compaction of the Pliocene-Quaternary sediments of the

Baku Archipelago on the basis of their facies characteristics. By considering the delineated intervals of the section as zones of lithification in the transformation of the investigated deposits under the influence of increases in compacting pressure from 0 to 150-250 kg/cm² and increases in temperature from 10 to 31°C, six steps can be distinguished. The results of the factor analysis and the lithological data presented above allow us to group these steps according to the characteristics of the processes taking place within them during two stages of lithogenesis: diagenesis and catagenesis.

The phase of diagenesis is characterized by intense dehydration and compaction of the sediments. It takes place in three steps during a change in pressure from 0 to 24 kg/cm² and a change in temperature from 10 to 15°C; it includes deposits to a depth of 250 m.

During the stage of catagenesis, the deposits change to the solid state and the intensity of their dehydration and compaction decreases significantly. The characteristics of this stage include the formation and development of direct (dry) contacts within the rock, beginning with transitional (point) and then phase-type contacts [6], and the formation of a microtexture oriented in the bedding plane. The transition from the stage of diagenesis to the stage of catagenesis is fairly evident in zone IV of lithification (250-550 m) on the basis of the transition of the deposits to the solid state, on the basis of the orientation of clay particles in the bedding plane, and on the basis of the sharp increase in the strength of the rock. This allows step IV of the lithogenesis to be considered as a transition between dia- and catagenesis, since this step accommodates the rock to the thermobaric conditions associated with catagenesis. Apparently, pressures and temperatures above 25 kg/cm² and 15°C, existing at step IV of lithogenesis, prove to be critical for the clay deposits under consideration; at such temperatures, a radical restructuring of the microtexture takes place within the deposits. These transformations could also be caused by some increase in effective (compacting) pressure resulting from the pressure of the columns of marine and pore water beginning to directly influence the framework of the ground and by a partial disappearance of the suspension effect. A necessary condition for this would be the formation of water-impermeable clay deposits which would disrupt the connection between the water enclosed in the rock and the water of the basin. The rocks of lithification zone IV would satisfy this conditions completely. As a result of these processes, the effective pressure could gradually increase, almost by a factor of 2; and values of 250 kg/cm², rather than 150 kb/cm², could be reached at a depth of 1255 m. Thus, steps V and VI of the lithification correspond to the earliest phase of catagenesis. The rocks of this phase prove to be very resistant to changes in pressure, but the temperature still does not exceed 31°C.

If the investigated section of clay deposits of the Baku Archipelago is represented as an upper portion of the lithosphere and the post-sedimentational transformation of the deposits is considered a result of the interaction of two geospheres, the hydrosphere and the lithosphere, the results presented above allow us to consider the zone of diagenesis as a zone of intersection of these two geospheres within water areas. It is logical that processes taking place in the hydrosphere would predominate during the phase of diagenesis and that processes taking place in the lithosphere would predominate during the stage of catagenesis. This interpretation of the two stages of lithogenesis is in accordance with one of the principles involved in the classification of sedimentary rocks on a quantitative basis, revealing the structure of relationships between all elements of the rock, even including genetic characteristics. In one case, we will have deposits with the fluid phase predominating within their composition; in the other case, we will have deposits with the solid phase predominating. Conclusions of such nature allow hope that classifications of sedimentary results can be constructed on a quantitative basis revealing the structure of relationships between all elements of the rock and even genetic features. The creation of a quantitative classification of this nature would be applicable in the future to multivariate statistical methods for lithological-facies and then formational analyses (the theoretical basis for such analyses was developed in [7, 8]).

In conclusion, it is best to emphasize that the results obtained not only substantiate the modern theory of lithogenesis, which serves as a basis for setting up problems for mathematical modelling, but also significantly broadens this theory. Moreover, the results allow us to concretize the posing of problems for further investigations.

LITERATURE CITED

1. A. E. Babinetz, V. A. Emel'yanov, A. Yu. Mitropol'skii, et al., The Physical-Mechanical Properties of the Sediments of the Black Sea [in Russian], Nauka Dumka, Kiev (1981).

2. K. G. Iereskog, D. I. Klován, and R. A. Reiment, Geological Factor Analysis [in Russian], Nedra, Leningrad (1982).
3. P. N. Kuprin, A. S. Shatov, V. G. Shlykov, et al., "Zonality in the alternation of properties of bottom deposits of the Caspian Sea along section," in: Joint Investigations of The Caspian Sea, Moscow State University, No. 5, 107-125 (1967).
4. A. S. Polyakov, "The formation of the physical-mechanical properties and changes in the microtexture of marine clay deposits during the process of lithogenesis," Vestn. Mos. Gos. Univ. Ser. Geol., No. 4, (1975).
5. A. S. Polyakov, V. I. Osipov, V. F. Kotlov, and P. N. Kuprin, "Changes in microtexture and physical-mechanical properties of clay deposits of the Baku Archipelago at the transition from the phase of diagenesis to the phase of catagenesis," Izv. Geol., No. 5, 29-40 (1979).
6. E. M. Sergeev, V. I. Osipov, and V. T. Trofimov, "The interaction of solid and fluid components and the dynamics of ground properties," in Groundwater and the Evolution of the Lithosphere [Russian translation], Nauka, Moscow (1985).
7. P. P. Timofeev, The Jurassic Coal-Bearing Formation of Southern Siberia and the Conditions of Its Creation [in Russian], Nauka, Moscow (1970).
8. P. P. Timofeev, "Some questions concerning the lithological-facies analysis of sedimentary deposits," in: Problems of Lithology and Geochemistry of Sedimentary Rocks and Ores [in Russian], Nauka, Moscow (1975).

THE PROBLEM OF THE INTERRELATIONSHIPS BETWEEN VITRINITE
REFLECTANCE AND THE LITHOLOGICAL CHARACTERISTICS
OF SEDIMENTARY ROCKS

A. N. Fomin

UDC 552.13

In the article, the rates of coalification of organic matter in various lithological types of rock are discussed. A generalization of the published data and the author's own observations do not allow unequivocal inferences to be made concerning the influence of lithology upon the changes in the reflectance of vitrinite. The small variations in this parameter observed, both increases and decreases, are within the boundaries of the stages and often lie within the limits of precision associated with the method of investigation.

The lithification of sedimentary strata is of major significance when evaluating possible oil and gas content. There are a number of methods which can be used for establishing the nature of transformations associated with sedimentary strata. The most convenient methods to implement are coal-petrographic methods based on the burial of organic material in rocks, organic material which, as a consequence of its specific chemical composition and structure, is sensitive to thermobaric influences. Traces of catagenetic alterations are therefore more evident within such components than within the mineral components of the rock. This property of organic material (OM) has been recently used to solve problems associated with determining the degree of transformation of sedimentary rocks. At present, the most precise, and therefore most widely used method is identification of stages of catagenesis on the basis of the reflectance of OM microcomponents. Most often, this method is carried out using the reflectance of vitrinite, a microcomponent well represented in rocks over a broad stratigraphic range (from Devonian to Neogene) and displaying a regular pattern of changing optical and chemical properties over the course of coalification.

Investigators have a variety of points of view concerning the causes of the transformation of OM. The preeminent role of temperature in the processes associated with carbonization of OM can be clearly traced on the basis of the kinetics of chemical reactions. The role of temperature is graphically confirmed by the anomalously high catagenesis of OM in

Institute of Geology and Geophysics, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk. Translated from *Litologiya i Poleznye Iskopaemye*, No. 4, pp. 74-83, July-August, 1989. Original article submitted June 6, 1988.

TABLE 1. Reflectance of Vitrinite (R^0) in Various Lithological Types of Rock, %

Region, deposit	Sand	Clay	Coal	Stage of lithogenesis
Prebaltic	0,15	0,17	0,18	Peat
Dnieper Basin	0,21	0,21-0,24	0,24-0,28	B
Kuzbass, Bogoslov	0,29	0,38	0,42	B
Georgia Tkibulsk	0,73	0,83	0,90	D-G
Georgia Tkvarchel'skoe	0,82	-	1,05	D-G

TABLE 2. Chemical and Optical Characteristics of OM in the Rocks of the Angren Lignite Deposit

Rock	Element composition, %		Refractive index of vitrinite
	C	O	
Sandstone	66-68	27-29	1,69
Claystone	69-71	24-26	1,71
Coal	71-75	21-24	1,72

zones of contact between sedimentary rock and magmatic bodies. The majority of investigators, therefore, believe that the catagenesis of OM is primarily controlled by increases in temperature within the sedimentary strata. It is true that other authors attribute major significance to the roles of such factors as pressure, time, the circumstances associated with the burial of the organic material, the lithological composition of the enclosing rocks, etc, or some combination of such factors. It is understandable that a definitive explanation of the principles behind the catagenesis of OM would be of significant interest.

However, the role of individual factors is still under discussion. Also, the question of the influence of the lithological composition of the rock upon the rate of carbonization of the OM buried within it has not been finally settled. Some investigators, interpreting the results of optical and chemical analyses; have traced no connections between changes in the parameters of OM and lithology and believe that the lithology displays a random character dependent upon a number of factors; others point to a pattern of changes in the characteristics of OM within the series sandstone-claystone-coal.

P. P. Timofeev and L. I. Bogolyubov [11] investigated the gelification of wood over a comparatively broad range of lithification (from peat to coals) from various lithological types of rock belonging to the deposits of deltaic, fluvial, back-water, lacustrine-marsh, and marsh facies (Table 1).

On the basis of these data, one can trace an increase in the mean reflectance values in the series sandstone-claystone-coal. According to the scale of catagenesis, this difference in values corresponds roughly to a demi-stage. These authors noted a similar character of coalification when studying the OM in rocks of the Angren lignite deposit [10]. An increase in the transformation of the OM from sandstones to coals was identified here, although the differences in the parameters were very minor and occurred primarily within the limits of precision of the methodologies used (Table 2).

P. P. Timofeev and L. I. Bogolyubov associate the observed variations in vitrinite reflectance and other parameters with influences of the lithological compositions of the rocks and the conditions surrounding their formation. Thus, the accumulation of sandstones took place in alluvial-deltaic environments, the accumulation of claystones took place in lacustrine-blockwater environments, and the accumulation of coal took place in marsh environments. It is known that plant remains falling within different paleogeographic depositional environ-

TABLE 3. Chemical and Optical Characteristics of the Tkibuli Deposit (coals of stage D)

Rock	C ^r , %	N _r	R ^a , %
Sandstone	80,3-83,1 81,8	< 1,795	6,6-7,0
Claystone	79,5-84,4 80,6	1,795-1,804	7,0-8,2
Coal	82,8-84,2 83,6	1,797-1,804	8,0-9,0

Explanation. Limits of coal content are presented in the denominator and mean values are presented in the numerator.

ments with specific paleohydrodynamic regimes undergo different conversions. When studying the Angren coal, in particular, it was noted that, according to chemical indices, telinite occurring within porous sandstone was more oxidized than monotypic microcomponents within claystone [8]. This can be explained by the fact that oxygen sorbed by the groundwaters in the porous environment of a sandstone has more significant effect on organic remains than oxygen in the environment of a claystone. As is well known, the effects of oxidative processes more frequently lead to an increase in vitrinite reflectance. In clay deposits, most frequently possessing poor filtration qualities, plant remains are better isolated from the influence of the aqueous medium and are therefore well preserved.

The environment associated with the formation of deposits can vary even within a single bed. In this connection, monotypic microcomponents at various sites within such a bed will differ in optical and chemical characteristics. It was thus found that vitrinite in coals of the durain type possesses a higher reflectance than does vitrinite in clarain and vitrain types. Coals of the durain type were formed in circulating waters within which partial oxidation of lignin-cellulose tissues took place because of the supply of free oxygen. The formation of clarains and vitrains coincided with stagnate water bodies with reducing environments favorable for the preservation of fragments from the destructive effects of oxidative processes. Three types of vitrinite can be distinguished, ranging from strongly to weakly reduced depending upon the original material and the conditions of formation associated with the deposit. The latter type is identifiable by higher reflectance values [6]. This is graphically evident from a comparison of the vitrinite reflectances in boghead and in typical humic coals. In the former, the sapropel environment of formation lowers the rate of coalification somewhat [2].

In addition to "facies" factors and, possibly, differences in original material, the physical inhomogeneity of fusain coals could have an effect upon the variation in reflectance at sites of vitrinite located between fusain microcomponents. This phenomenon has been referred to be N. M. Krylov and optical anomalies [6]. The phenomenon is expressed in small local increases in anisotropy and vitrinite reflectance occurring at contacts and sometimes around certain "hard" components which are fusain fragments and mineral particles. In the presence of large quantities of "hard bodies" in coal, the sites of vitrinite locked between such bodies are compacted, acquire a molecular ordering, and, in connected with this, become more anisotropic, with high reflectances. Such phenomena are most characteristic of tectonically active regions with deposits which have been subject to substantial dynamic loads.

From the results of the investigations of G. M. Parparov, who studied coal detritus from the Mesozoic deposits of the Surgut region, it follows that the rate of coalification of vitrinitized remains increases within the series sandstone-claystone-coal and depends, to a certain degree, upon the size of the fragments. In particular, the refractive index of vitrinite in insoluble OM from claystones not containing visually identifiable coal inclusions is usually 0.015-0.020 higher than in macrodetritus from monotypic samples at the same depth interval [5]. In the opinion of V. A. Uspenskii, these types of differences in refractive indices between vitrinites from micro- and macrodetritus can probably be the somewhat different conditions of their burial and transformation. It is possible that bits of OM are partially oxidized during transport. Such oxidation, as is well known, most often brings

TABLE 4. Reflectance of Vitrinite in Various Lithological Types of Rock

Deposit or borehole	Rock	Sampling interval, m	Reflectance, %		Stage of catagenesis
			R ^a	R ^o	
1	2	3	4	5	6
Trans-Baikal					
Kharanorskoe	Clay	Kar'er	6,4	—	B
	Coal	"	6,7	—	"
Tigninskaya	Claystone	"	6,0	—	"
	Coal	"	6,4	—	"
South-western Siberian platform					
Vanzhil'skaya-1	Sandstone	1784-1786	6,3	0,35	"
	Siltstone		6,4	0,37	"
	Coal	1417-1426	6,6	0,40	"
Chkalovskaya-5	Sandstone		7,1	—	E
	Coal	2594-2598	7,0	—	"
Chagvinskaya-1	Claystone	2771-2775	7,1	—	"
	Coal		7,0	—	"
Parbig'skaya-1	Sandstone	2691-2694	7,2	—	"
	Claystone		7,2	—	"
Sel'veikin'skaya-2	Siltstone	2616-2623	7,1	—	"
	Coal		7,3	—	"
Severo-Lyubel'skaya-2	Sandstone	2195-2199	7,2	—	"
	Coal	2134-2138	6,9	—	"
Yubileinaya-404	Sandstone	2459-2464	7,0	—	"
	Claystone	2607-2511	7,4	—	"
Nyarginskaya-1	Siltstone	2314-2335	7,6	—	D
	Claystone		8,2	—	"
	Coal	2600-2605	7,0	—	E
Mozhanskaya-1	Siltstone		7,8	—	D
	Claystone	2480-2490	7,8	—	"
	Siltstone		—	0,87	"
Verkhnesalatskaya-25	Claystone	3195-3199	—	0,80	"
	Sandstone		—	—	"
Nyul'gin'skaya-1	Coal	3084-3089	7,5	—	ED-D
	Clay	2382-2384	6,7	—	BE
Verkhnekarzinskaya-1	Coal	2507-2511	7,4	—	E
	Clay	2828-2836	8,0	—	B
Nizhnetabaganskaya-4	Coal	2876-2886	7,8	—	"
	Sandstone	3100-3109	7,1	—	E
	Coal	3093-3100	7,3	—	D
	"	3130-3132	7,9	—	E
Yuzhno-Urman'skaya-1	Siltstone	3085-3090	7,4	—	"
	Coal	3140-3147	8,0	—	D
Pogranichnaya-2	Siltstone	2671-2678	8,1	—	"
	Claystone		8,2	—	"
	Coal	2525-2531	8,0	—	"
Protochnaya-2	Sandstone	2781-2800	7,7	—	"
	Coal		8,1	—	"
Severo-Otainskaya-9	Sandstone	2828-2836	7,8	—	"
	Coal		7,8	—	"
Kalinovaya-12	Siltstone	2660-2626	7,3	—	E
	Claystone		7,9	—	D
	Coal	2581-2593	7,6	—	"
Krylovskaya-2	Sandstone		7,5	—	ED-D
	Claystone	2587-2593	7,9	—	E
	Sandstone		8,0	—	"
Chkalovskaya-7	Claystone	2642-2658	7,5	—	ED-D
	Coal		7,9	—	E
Lesnaya-206	Siltstone	2446-2451	7,2	—	D
	Claystone		7,6	—	E
Chimulyak'skaya-1	Siltstone	2505-2510	—	0,70	"
	Claystone	3048-3069	—	0,90	EG-G
Chkalovskaya-3	Sandstone	3104-3122	—	1,14	"
	Claystone	3095-3100	—	0,95	"
	Coal	3176-3183	—	1,0	EG-G
Nikol'skaya-1	Claystone	8,5	8,6	—	EG-G
	Coal		8,6	—	"

Table 4 (continued).

1	2	3	4	5	6
Srednenyuro1'skaya-45	Sandstone	2697-2603	12,0	-	T-PA
	Claystone		14,1	-	A
Kolpashevskaya-7	Sandstone	2836-2839	12,8	-	PA
	Claystone		13,0	-	"
Vostochno-Nikol'skaya-1	Claystone	4496-4500	13,1	-	PA-A
	"	4460-4475	12,0	-	T-PA
	Coal	4399-4412	12,3	-	PA

about increases in reflectance and in the index of refraction. Moreover, macrodetritus forms mechanical inclusions within the rock during burial, whereas microdetritus probably is present in a state similar to the sorbed state and possibly is altered somewhat more than macrodetritus under the catalytic influence of the mineral particles of the rock [14].

Thus, a series of investigators believe that vitrinite reflectance in claystones and coals is greater than in sandstones. However, this dependence is not always clearly traceable, due to various factors: peculiarities of the original plant material of the vitrinite, the microbiological alterations of this material, oxidation, etc. Fairly numerous deviations from this scheme were noted by I. I. Ammosov [1], who pointed out several possible causes for these phenomena. Generally agreeing with the pattern found, he noted that the pattern was discovered primarily on the basis of averaged data which overlap with one another for different types of rocks.

N. Bostick and G. Foster carried out a fairly complete, general investigation of these questions on the basis of material from the carbonate deposits of the Illinois basin. They point out that they were not able to trace a direct influence of the lithological composition of the rocks upon indices of catagenesis for DOM (dispersed organic matter). The authors explain the absence of a clear pattern by means the following factors: different types of plant associations, different levels of gelification or biochemical coalification during diagenesis, different rates of catagenetic reactions associated with different properties of accessory minerals, different permeabilities of rocks and quantitative contents of OM within them [15].

It should be noted that the conclusions of individual investigators concerning this question are not entirely convincing. Thus, B. K. Chichua [12], whose work is often cited during discussions of this question, presents the following results from an investigation of the vitrinite in the deposits of the Tkibuli coal deposit (Table 3).

Judging from this data, fairly significant variations in vitrinite reflectance are apparent. These variations correspond to stages B-E in sandstones and stages D-G in coals. But, at the same time, the slight differences in the content of carbon C^F and index of refraction N_r of vitrinite in various rocks are not in agreement with these data. Moreover, substantial variations in the optical and chemical parameters of vitrinite can be found in monotypic rocks. All this raises doubts concerning how representative the data of investigation really is; the data can hardly serve as proof of an effect of lithological composition upon the rate of coalification of OM. Especially since P. P. Timofeev and L. I. Bogolyubov, studying analogous rocks of this same deposit, found a difference in vitrinite reflectance R^0 between sandstones and coals equalling only 0.17%, i.e., the discrepancy in the data does not exceed the limits associated with a single stage [11].

In a more recent report using a study of the coal-bearing deposits of Georgia and Donbass, B. K. Chichua et al. showed that the properties of vitrinite from different lithological types of rock are approximately the same in similar zones of catagenesis. In some cases, the vitrinite from sandstones and claystones is characterized by a somewhat low index of refraction; in other cases, the reverse is true. Similar values are often encountered for this parameter. On the basis of the materials studied, these investigators arrived at the conclusion that primary lithological-facies factors have no substantial influence over the formation of the optical properties of vitrinite over the entire range of catagenesis (stages B-A) [13].

The numerous measurements of vitrinite reflectance (homogeneous collinite) which we carried out for the Mesozoic deposits of the Western Siberian platform (to a lesser degree for deposits of other regions and other ages) does not allow us to form a definitive conclusion in favor of a connection between vitrinite reflectance and the lithological type of rock. For the investigation, samples were taken from a narrow depth interval (usually differences of several meters were involved) in order to avoid the influence of both regional and local

TABLE 4. Reflectance of Vitrinite in Various Lithological Types of Rock

Deposit or borehole	Rock	Sampling interval, m	Reflectance, %		Stage of catagenesis
			R ^a	R ^o	
1	2	3	4	5	6
Trans-Baikal					
Kharanorskoe	Clay	Kar'er	6,4	—	B
	Coal	"	6,7	—	"
Tigninskaya	Claystone	"	6,0	—	"
	Coal	"	6,4	—	"
South-western Siberian platform					
Vanzhil'skaya-1	Sandstone	1784-1786	6,3	0,35	"
	Siltstone		6,4	0,37	"
	Coal	1417-1426	6,6	0,40	"
Chkalovskaya-5	Sandstone		7,1	—	E
	Coal	2594-2598	7,0	—	"
Chagvinskaya-1	Claystone	2771-2775	7,1	—	"
	Coal		7,0	—	"
Parbigskaya-1	Sandstone	2691-2694	7,2	—	"
	Claystone		7,2	—	"
Sel'veikin'skaya-2	Siltstone	2616-2623	7,1	—	"
	Coal		7,3	—	"
Severo-Lymbel'skaya-2	Sandstone	2195-2199	7,2	—	"
	Coal	2134-2138	6,9	—	"
Yubileinaya-404	Sandstone	2459-2464	7,0	—	"
	Claystone	2607-2511	7,4	—	"
Nyarginskaya-1	Siltstone	2314-2335	7,6	—	D
	Claystone		8,2	—	"
	Coal	2600-2605	7,0	—	E
Mozhanskaya-1	Siltstone		7,8	—	D
	Claystone	2480-2490	7,8	—	"
Verkhnesalatskaya-25	Siltstone		—	0,87	"
	Claystone	3195-3199	—	0,80	"
Nyul'ginskaya-1	Sandstone		7,5	—	ED-D
	Coal	3084-3089	6,7	—	BE
Verkhnekazinskaya-1	Clay	2382-2384	7,4	—	E
	Coal	2507-2511	8,0	—	B
Nizhnetabaganskaya-4	Clay	2828-2836	7,8	—	"
	Coal	2876-2886	7,1	—	E
	Sandstone	3100-3109	7,6	—	"
	Coal	3093-3100	7,1	—	D
	"	3130-3132	7,3	—	E
Yuzhno-Urman'skaya-1	Siltstone	3085-3090	7,9	—	"
	Coal	3140-3147	7,4	—	D
Pogranichnaya-2	Siltstone	2604-2615	8,0	—	E-ED
	Claystone		8,1	—	"
	Coal	2671-2678	8,2	—	"
	Sandstone		8,2	—	"
Protochnaya-2	Coal	2525-2531	7,8	—	"
	Sandstone	2781-2800	8,0	—	"
Severo-Otanskaya-9	Coal		7,7	—	"
	Sandstone	2828-2836	8,1	—	"
Kalinovaya-12	Coal		7,8	—	"
	Coal	2660-2626	7,8	—	"
Kalinovaya-22	Siltstone		7,3	—	E
	Claystone	2581-2593	7,9	—	D
	Coal		7,6	—	"
Krylovskaya-2	Sandstone	2587-2593	7,5	—	ED-D
	Claystone		7,9	—	E
Chkalovskaya-7	Sandstone	2587-2593	8,0	—	"
	Claystone		7,5	—	ED-D
	Coal	2642-2658	7,9	—	E
Lesnaya-206	Siltstone		7,2	—	D
	Claystone	2446-2451	7,6	—	E
	Siltstone		—	0,70	"
Chimulyakskaya-1	Claystone	2505-2510	—	0,90	"
Chkalovskaya-3	Sandstone	3048-3069	—	1,14	EG-G
	Claystone	3104-3122	—	0,95	"
	Coal	3095-3100	—	1,0	EG-G
Nikol'skaya-1	Claystone	3176-3183	8,5	1,0	EG-G
	Coal		8,6	—	"

Table 4 (continued).

1	2	3	4	5	6
Srednenyuro- skaya-45	Sandstone	2697-2603	12,0	-	T-PA
	Claystone		14,1	-	A
Kolpashev- skaya-7	Sandstone	2836-2839	12,8	-	PA
	Claystone		13,0	-	"
Vostochno- Nikol'skaya- 1	Claystone	4496-4500	13,1	-	PA-A
	"	4460-4475	12,0	-	T-PA
	Coal	4399-4412	12,3	-	PA

about increases in reflectance and in the index of refraction. Moreover, macrodetritus forms mechanical inclusions within the rock during burial, whereas microdetritus probably is present in a state similar to the sorbed state and possibly is altered somewhat more than macrodetritus under the catalytic influence of the mineral particles of the rock [14].

Thus, a series of investigators believe that vitrinite reflectance in claystones and coals is greater than in sandstones. However, this dependence is not always clearly traceable, due to various factors: peculiarities of the original plant material of the vitrinite, the microbiological alterations of this material, oxidation, etc. Fairly numerous deviations from this scheme were noted by I. I. Ammosov [1], who pointed out several possible causes for these phenomena. Generally agreeing with the pattern found, he noted that the pattern was discovered primarily on the basis of averaged data which overlap with one another for different types of rocks.

N. Bostick and G. Foster carried out a fairly complete, general investigation of these questions on the basis of material from the carbonate deposits of the Illinois basin. They point out that they were not able to trace a direct influence of the lithological composition of the rocks upon indices of catagenesis for DOM (dispersed organic matter). The authors explain the absence of a clear pattern by means the following factors: different types of plant associations, different levels of gelification or biochemical coalification during diagenesis, different rates of catagenetic reactions associated with different properties of accessory minerals, different permeabilities of rocks and quantitative contents of OM within them [15].

It should be noted that the conclusions of individual investigators concerning this question are not entirely convincing. Thus, B. K. Chichua [12], whose work is often cited during discussions of this question, presents the following results from an investigation of the vitrinite in the deposits of the Tkibuli coal deposit (Table 3).

Judging from this data, fairly significant variations in vitrinite reflectance are apparent. These variations correspond to stages B-E in sandstones and stages D-G in coals. But, at the same time, the slight differences in the content of carbon C^x and index of refraction N_r of vitrinite in various rocks are not in agreement with these data. Moreover, substantial variations in the optical and chemical parameters of vitrinite can be found in monotypic rocks. All this raises doubts concerning how representative the data of investigation really is; the data can hardly serve as proof of an effect of lithological composition upon the rate of coalification of OM. Especially since P. P. Timofeev and L. I. Bogolyubov, studying analogous rocks of this same deposit, found a difference in vitrinite reflectance R^0 between sandstones and coals equalling only 0.17%, i.e., the discrepancy in the data does not exceed the limits associated with a single stage [11].

In a more recent report using a study of the coal-bearing deposits of Georgia and Donbass, B. K. Chichua et al. showed that the properties of vitrinite from different lithological types of rock are approximately the same in similar zones of catagenesis. In some cases, the vitrinite from sandstones and claystones is characterized by a somewhat low index of refraction; in other cases, the reverse is true. Similar values are often encountered for this parameter. On the basis of the materials studied, these investigators arrived at the conclusion that primary lithological-facies factors have no substantial influence over the formation of the optical properties of vitrinite over the entire range of catagenesis (stages B-A) [13].

The numerous measurements of vitrinite reflectance (homogeneous collinite) which we carried out for the Mesozoic deposits of the Western Siberian platform (to a lesser degree for deposits of other regions and other ages) does not allow us to form a definitive conclusion in favor of a connection between vitrinite reflectance and the lithological type of rock. For the investigation, samples were taken from a narrow depth interval (usually differences of several meters were involved) in order to avoid the influence of both regional and local

TABLE 5. Thermophysical Properties of Sedimentary Rocks and Fluids [9]

Rock, fluid	Thermoconductivity, V/m·deg	Thermoconductivity, J/kg·deg	Rock, fluid	Thermoconductivity, V/m·deg	Thermoconductivity, J/kg·deg
Sandstone	1,81	925	Rock salt	3,64	2557
Siltstone	1,65	894	Peat	0,07	1758
Claystone	1,32	846	Rock salt	0,45	1160
Clayey shale	2,34	982			
			Anthracite	0,59	—
Dolomite	3,24	1088	Air	0,026	1007
Limestone	2,37	897	Water	0,61	4180
Marl	1,96	1908	Oil	0,14	2093

factors associated with catagenesis. It should be noted that the Western Siberian platform is an especially suitable object for investigating this question. Sandy-silty and clayey deposits containing OM both in concentrated and in disseminated forms are widely represented in the sedimentary complex. Moreover, DOM transformed within stages ranging from G-A is found in the Pre-Jurassic terrigenous-carbonate strata. In order to study the less coalified OM, we collected rocks of various lithological types (each of which was formed under similar conditions) of Jurassic age from the Western Siberian platform and also from several lignite deposits of the Trans-Baikal (the Kharanorsk, Tigninsk, and Gusinozersk deposits). The measurements of vitrinite reflectance were carried out on a POOC-1 photoelectronic apparatus at a wavelength of 546 nm in air R^a and immersion A^o environments. Polished sections prepared from intact rock without preliminary enrichment were used for the investigation. In this way, we avoided the effects of strong acids upon the optical characteristics of the organic remains which occur when dissolving the mineral portion of the rock.

On the basis of our observations, we were not able to trace a clear dependence of vitrinite reflectance upon the lithological composition of the rock for the transformation of OM from stage B to stage A (individual results are presented in Table 4). In some cases, an increase in vitrinite reflectance from sandstones to coals was noted; in other cases, a decrease in these values was observed. In regions of lignite deposits in Trans-Baikal, R^a was 0.3-0.4% higher than in the clay deposits. Similar results were obtained over the Vanzhil'sk area of the Western Siberian platform. Different results were noted in deposits of this region with catagenesis at stage E. The vitrinite reflectances in coals here in the Chkalovsk, Chagvinsk, Parbigsk, and other areas are either the same as in other rocks or are even lesser. Only in the Yubilein area is R^a in the coals 0.4% higher than in sandstones.

Of the 17 prospecting areas considered in which OM was transformed up to stage D, some increase in vitrinite reflectance within the series sandstone-claystone-coal was noted in only seven. Whereas an inverse dependence could be traced in five, no connected with the lithological composition of the rock could be detected in the remaining five. Thus, R^a in claystone within the Kalinov region is 0.6% higher than in siltstone and is 0.3% higher than in coals at the same time. Within the Chkalovsk area, R^o in coal is 0.4% higher than in claystone, but is 0.1% than in sandstone.

Deposits with catagenesis in stage G were studied in the Nikol'sk and Chkalovsk areas. In the first of these areas, R^o in coals is 0.1% higher than in claystones; in the second, these values are practically equivalent (1.0 and 0.95). The value of R^o in the sandstones is significantly higher (1.15%). The OM of Paleozoic deposits existing at the same stages of apocatagenesis was studied from three prospecting areas. Roughly equivalent values for sandstones and claystones (12.8 and 13.0% respectively) were noted in the Kolpashevsk area. In the Srednyurol's area, this difference was fairly substantial (12.0 and 14.1%) and was expressed over the entire stage of catagenesis. It is difficult to trace to interrelationship between vitrinite reflectance and lithological composition of the rock in the Eastern Nikol'sk area. In individual samples of claystones here, the vitrinite reflectance is substantially higher than in coals; in other cases, the vitrinite reflectance is lower than in coals.

Thus, one can thus not always trace a dependence of vitrinite reflectance upon the lithological type of rock in the materials we have presented. However, considerations of the roles of sandstones, claystones, and coals are far from being satisfactory for answering questions concerning the rates of coalification of isometamorphic vitrinite. Observations show that particles of vitrinite with differing optical characteristics can be found even in

sandstones with almost identical lithological compositions, just as in other rocks. Possibly, the thermoconductivity and heat capacity of the rock is of more value for explaining the differences in vitrinite reflectances than are the grain-size and mineral-petrographic compositions of the rock. It is well known that fuel resources, inorganic rocks, minerals, and fluids possess different values for these parameters (Table 5). For example, rocks with ferruginized veins accompanied by inclusions of pyrite, siderite, calcite, or other minerals which are good heat conductors are characterized by higher values of thermoconductivity. It is therefore not surprising that the transformation of OM within one and the same lithological type of rock will be greater when the pyrite content is significantly higher.

The intensity of the heat transfer in rocks depends upon the chemical compositions of the rocks, density, temperature, crystal structure, etc. In general, the thermoconductivity decreases as the compactness of the crystal stacking in the rocks becomes less. In sedimentary rocks, the decisive factor determining thermoconductivity is not so much the properties of the solid framework as the conductivity of the filler in the intergranular medium air, water, oil, etc. The grains of sea and ocean deposits most saturated with moisture are distinguished by clearly lower thermoconductivity and the high heat capacity. Oil-saturated sedimentary rocks usually show significantly lower values of thermoconductivity when compared to monotypic water-saturated sedimentary deposits [4].

The thermoconductivity of rock gradually falls with decreasing grain-size, this can be explained by a weakening of convective transport of heat by water, by retention of heat in the strata, and by an increase of contact thermoconductivity in microporous structures. It would be quite reasonable to anticipate, in this connection, that the rate of coalification of OM would increase within the series sandstone-claystone-coal. This can be observed within the stages of protocatagenesis (stage B). But, as was pointed out above, a number of other factors capable of influencing the intensity of the carbonization of the OM to one degree or another could be superimposed upon this.

The degree of lithification of sedimentary deposits turns out to have a significant effect upon thermophysical characteristics. In particular, thermoconductivity is substantially lower in terrigenous rocks. A clear dependence has not been found for carbonates. Dense, microgranular limestones and dolomites with inclusions of highly thermoconductive minerals possess the highest coefficients of thermoconductivity among the deposits. Limestones, dolomites, rock salt, and other chemogenic sedimentary rocks differ from terrigenous rocks in having significantly higher thermoconductivities (see Table 5); heat is weakly retained in these strata and slow rates of coalification are observed. On the basis of interpretations of data on variations in the quantity and quality of DOM, bitumoids, and hydrocarbons during the lithogenesis of carbonate rocks, a series of investigators have thus noted that the intensity of generation and migration of hydrocarbons in these strata is shifted relative to that in clayey strata within deeper zones of catagenesis [3]. Also, the small content or absence of clay minerals, catalysts in processes of oil formation, possibly contributes the slow intensity of transformation of OM in carbonate rocks. The thermoconductivities of carbonate and saline rocks decrease with increasing content of sandy-clayey material, but marls and chalks are similar to terrigenous deposits with respect to this parameter.

On the basis of theoretical considerations, the lithological composition of the rock should have a very important effect upon the depth zonality associated with the catagenesis of organic plant remains. As is well known, the heat flux within sedimentary strata exists in direct relationship to the geothermal gradient and thermoconductivity of the rock. It follows from this that the geothermal gradients will be inversely proportional to the thermoconductivity of the rock for identical intensities of heat flux. Since salts possess the highest thermoconductivities and caustophytoliths possess the lowest (see Table 5), the geothermal gradients and, consequently, the depth zonality associated with catagenesis of OM in the presence of identical heat fluxes and monotypic rock compositions (coals, salts) should be different: they should be shortened in coals and extended in salts. In nature, however, there are generally no strata composed of a single type of rock, but there are almost always rocks with similar thermoconductivities in a section. To a large degree, it is therefore impossible to trace the influence of the lithological composition of the rock upon the depth zonality associated with catagenesis of OM. Regions where thick saline strata occur could be an exception.

Salts, possessing significantly appreciable thermoconductivity in comparison with enclosing terrigenous rocks and breaching sedimentary strata, apparently play the role of a unique

heat-exchanger over the entire duration of growth with respect to cupolas. A portion of the heat is disseminated into the atmosphere during this process, and the remaining heat retained by the saline stratum itself is used up in endothermal reactions. The processes mentioned thus restrain the progress of carbonization; this is expressed in the anomalously low catagenesis of OM even at significant depths. Possibly, this is precisely why coalification of OM at stage G is noted at a depth of 7.0-7.5 km in the Emba region of the Pre-Caspian basin in the subsaline deposits and noted at a depth of 4.9 km in the Kenkiyansk region at stage E [7]. A similar situation is characteristic of a number of boreholes in the Sahara. Thus, G. Damberger pointed out in 1975 that there was a delay in the coalification within the sandstones due to their high thermoconductivities. The heat within the sandstones could be transferred out fast enough not to have any significant effect upon organic plant remains; catagenesis increases slowly with depth.

We have thus discussed various factors capable of having an influence, to one degree or another, on the transformation of OM. It is impossible to arrive at a definitive conclusion concerning a dependence of vitrinite reflectance upon the lithological type of rock on the basis of the accumulation of data presented. In individual cases, increases in vitrinite reflectance within the series sandstone-claystone-coal are noticeable; in other cases, there is no increase or the opposite situation is observed. The hypothesis of an influence of the lithological features of enclosing rocks upon the rate of coalification of OM arises in those cases when a clear increase within the series sandstone-claystone-coal can be identified. In actuality, however, the difference in values could be due not only to the influence of lithogenesis, but also to the fact that the vitrinite in sandstone is collinite, while the vitrinite in claystone is telinite. As is well known, such microcomponents lying in direct proximity to the same rock (including cases involving coal) differ somewhat in vitrinite reflectance. This is a consequence of peculiarities associated with the original material and the conditions of its conversion during diagenesis. Monotypic microcomponents should be compared in this regard order to clarify peculiarities associated with variations in vitrinite reflectance within various types of rock. Investigators (the authors included) most often use collinite for identification of the stages of catagenesis.

Some investigators rely upon data of chemical or technical analyses when discussing the role of the lithological composition of the rock upon the rate of coalification of OM. However, the precision of the results obtained by these methods is not very high, and one can only roughly infer the level of transformation of OM on such basis. One reason for this is probably the fact that samples of OM with the entire gamut of microcomponents (possessing different rates of alteration in their parameters during the course of coalification) must be collected for study. Conclusions concerning the catagenesis of OM made on the basis of these data are therefore frequently not in agreement with coal-petrographic data. It is better not to use the results of chemical and technical analyses to solve such a complex problem as the influence of the lithological characteristics of rocks upon the intensity of coalification of the OM trapped within them.

It is quite evident that a multitude of factors, either accelerating or slowing down the rate of coalification, affect OM during the burial period and during further alterations. Deviations of the vitrinite reflectance to one side or the other depend upon the sum total of such factors. One should certainly consider the possibility of fluctuations in this parameter when identifying the stage of catagenesis. However the observed (often minor) variations in vitrinite reflectance, both in diverse and in lithologically monotypic rocks most often do not exceed the boundaries associated with a stage and often lie within the limits of precision of the method of determination (see Table 4). Alterations in the properties of both disseminated and concentrated OM occur primarily under the influence of temperature and pressure. This permits broad application of variations in the optical properties of vitrinite for the identification of stages of catagenesis associated with practically any sedimentary rock containing plant remains. Taking care in making a qualitative selection of samples for study and establishing the degree of coalification of the basis of well preserved fragments of monotypic microcomponents formed in similar facies environments are all that is required.

LITERATURE CITED

1. I. I. Ammosov, "Lithification and oil content," Petrography of Coals and the Paragenesis of Fuel Resources [in Russian], Nedra, Moscow (1967), pp. 5-80.
2. N. I. Babinkova and G. S. Kalmykov, "The conversion of humus particles in a sapropelic environment (based on the Olenek boghead coal as an example)," in: Proceedings of the 3rd Geological Congress on Solid Fuel Resources, Rostov-on-Don (1967), pp. 28-30.

3. V. V. Ivanov and B. A. Klubov, "The mechanism of oil formation in carbonate rocks," *Izv. Akad. Nauk SSSR, Ser. Geol.*, 12, 99-106 (1977).
4. U. I. Moiseenko and A. A. Smyslov, *The Temperature of Oil in the Ground* [in Russian], Nedra, Leningrad (1986).
5. G. M. Parparova, "Metamorphism of organic matter in the Mesozoic deposits of the Surgut region," *Geol. Geofiz.*, No. 7, 11-23 (1966).
6. L. I. Sarbeeva and N. M. Krylova, "Vitrinite reflectance of coefficients of coals in a metamorphic series," in: *Problems Concerning the Morphology of Coals and the Epigenesis of Enclosing Strata* [in Russian], Nauka, Leningrad (1968).
7. V. S. Sobolev and G. M. Parparova, "The metamorphism of disseminated organic matter in the Paleozoic and Mesozoic deposits of the eastern portion of the Pre-Caspian basin in connection with the oil and gas content," *Dokl. Akad. Nauk SSSR*, 221, No. 3, 722-725 (1975).
8. I. S. Sofiev, I. A. Gorlenko, and I. N. Semasheva, "Some factors associated with the affect of the sedimentary environment upon the properties of coal microcomponents," *Dokl. Akad. Nauk SSSR*, 152, No. 2, 438-440 (1963).
9. *Handbook of Physical Constants of Rocks* [Russian translation], Mir, Moscow (1969).
10. P. P. Timofeev and L. I. Bogolyubova, "Features associated with the coalification of vitrinite in rocks and coals of the Angren lignite deposit," *Dokl. Akad. Nauk SSSR*, 151, No. 4, 938-944 (1963).
11. P. P. Timofeev and L. I. Bogolyubova, "Post-sedimentational alterations of organic matter as a function of lithological types of rocks and facies conditions associated with their deposition," in: *Organic Matter of Modern and Resource-Related Sediments* [in Russian], Nauka, Moscow (1971), pp. 160-190.
12. B. K. Chichua, "The problem of studying the initial metamorphism of sedimentary rocks in connected with their oil and gas content," *Azerb. Neft. Khoz-vo.* No. 7, 13-16 (1964).
13. B. K. Chichua, A. I. Suladze, and A. D. Kobakhidze, "Characteristics of the alteration of vitrinite reflectance in various lithological-facies types of rocks during the process of catagenesis," in *Problems of Geology and Metallogeny in the Caucasus* [in Russian], Metsniereba, Tbilisi (1976), pp. 259-365.
14. V. A. Uspenskii, "Organic matter and its role in processes associated with the evolution of sedimentary material," *Tr. Vses. Nauchn.-Issled. Geol. Inst.*, 261, 7-21 (1975).
15. N. H. Bostick and J. N. Foster, "Comparison of vitrinite reflectance in coal seams and in kerogen of a sedimentary section," *Petrogr. Matiere Org. Sediments*, in: *Relat. Paleo-temp. et Petrol.*, Paris (1975), pp. 13-25.

GLAUCONITE FORMATION CONDITIONS DURING THE PALEOGENE IN THE EASTERN MEDITERRANEAN BASED ON ISOTOPIC DATA

B. G. Pokrovskii and D. I. Golovin

UDC 553.679:551.781(262)

The paper discusses determinations of isotopic composition of oxygen, hydrogen, and carbon in glauconites and glauconite-bearing carbonate rocks of the Paleogene in Syria, previously dated by Rb-Sr- and K-Ar-methods.

Glauconite is a mineral actively used for radiologic dating of sedimentary rocks. However, isotopic datings often do not provide the age of sedimentation. Some of the datings are too "young," while others are too "old." Reliable interpretation of isotopic datings is closely related to glauconite genesis, especially to the contribution of hydrothermal processes, rewashing, redeposition, epigenesis, etc., to the development of glauconite isotopic systems [7, 20]. Some of these questions can in principle be solved by using stable isotopes which are extremely sensitive to temperature and composition variations of mineral-forming solutions.

Geological Institute, Academy of Sciences of the USSR, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 4, pp. 84-96, July-August, 1989. Original article submitted August 8, 1988.

TABLE 1. δD in Water Isolated During Stepped Heating of Glauconite in a Vacuum

Expt. number	Temp., °C	δD , ‰	H ₂ O, %	Expt. number	Temp., °C	δD , ‰	H ₂ O, %
1	100	-133	1.13	5	500	-95	0.95
2	185	-117	0.51	6	600	-90	0.66
3	300	-90	1.93	7	700	-83	0.16
4	400	-93	1.51				

Note. 1. Time of stay at each temperature 2 hr. 2. δD_{H_2O} in air during experiment was $-148^{\circ}/_{00}$.

TABLE 2. Effect of Preliminary Training of Evaluation of δD and H₂O Concentration in Glauconite (specimen 1040-2)

Training		Released at 1200°C		Training		Released at 1200°C	
specimen type	T, °C	δD , ‰	H ₂ O, %	specimen type	T, °C	δD , ‰	H ₂ O, %
Globules	185	-108.0	5.00	Globules	300	-109.0	3.15
Ground	185	-108.5	4.67	Ground	300	-109.0	2.77

OBJECT OF STUDY

We investigated the sections of Jebel-Hayan, Jebel-Abyad, Jebel-Antar, and wadi Harrar in the Palmyran folded zone near Tudmor Mountain (Palmyra). Detailed lithologic and micro-paleontologic descriptions of sections and development of the paleobasin of the area can be found in [2, 4-6, 8, 10].

Glauconite grains that form glauconite horizons of the section are a mix of three-dimensionally ordered glauconite 1M (sometimes 1Md) and smectite-glauconite mixed-layer phases with 20 to 40% of swelling layers. The proportion of the layers varies among horizons in globules of various density. No free smectite phase has been found.

The preservation of foraminifers in sediments between glauconite horizons is quite good. Secondary calcite sometimes grows on nannoplankton and foraminifers. Carbonate material of glauconite horizons is poor in microfossils. Most of these are benthic forms, but usually of poor preservation.

$\delta^{12}C$ and $\delta^{18}O$ were studied: a) in gross samples of carbonate glauconite-free rocks prepared for micropaleontological investigations and containing complete sets of planktonic foraminifers of each zone; b) in carbonate matrix ("cement") or glauconite horizons enclosing glauconite and represented by poorly preserved biogenic fragments and secondary calcite; and c) in sets of benthic foraminifers selected manually from carbonaceous glauconite-free rocks and rinsed in an ultrasound bath with distilled water.

In addition, the isotopic composition of oxygen and hydrogen were determined in glauconite itself.

METHOD OF INVESTIGATION

Calcite for isotopic analysis of carbon and oxygen was decomposed with H₂PO₄ and glauconite with ClF₃. Water for isotopic analysis of hydrogen was disintegrated with metallic uranium. Installations for specimen preparation have been described in [3].

The method of determination of isotopic composition of hydrogen in glauconite has certain specific features that should be explained. Besides hydroxyl water, whose isotopic composition reflects the mineral formation conditions in glauconite, it contains considerable amounts of interlayer and surface-sorbed water. Table 1 presents the results of determination of δD in water isolated by gradual glauconite heating in a vacuum. At 100°C the surface-sorbed and most of the interlayer water is apparently released. It is similar in isotopic composition to the water vapor of laboratory air. In the interval of 100-185°C much less water is released. This is probably the residue of interlayer water. It is noticeably enriched in deuterium (possibly, hydroxyl water begins to be isolated at this temperature). With continued heating, the isotopic composition remains virtually constant and probably characterizes the

TABLE 3. Results of a Study of K-Ar-Systems of Middle Eocene Glaucanites

Specimen number (section)	Zone	Sample number	Density fraction, g/cm ³	K conc., %	Ar conc., mm ³ /g	Calc. age, million years
52/83 (Arak)	P13	79	-	4.09	0.00527	32.0±0.6
		69	<2.5	4.06	0.001528	33.2±1.0
		70	2.5-2.6	4.51	0.00722	40.0±1.2
17/83 (Jebel-Hayan)	P12	71	2.6-2.7	5.21	0.00834	40.5±1.5
		72	2.7-2.8	5.64	0.01010	45.6±1.5
		73	2.8-2.9	4.77	0.00811	43.0±1.5
836* (Arak)	P12	-	2.45-2.7	4.70	0.0059	31.9±1.5
717* (Jebel-Hayan)		-	2.55-2.65	5.10	0.0065	32.5±1.5

*Borrowed from [8].

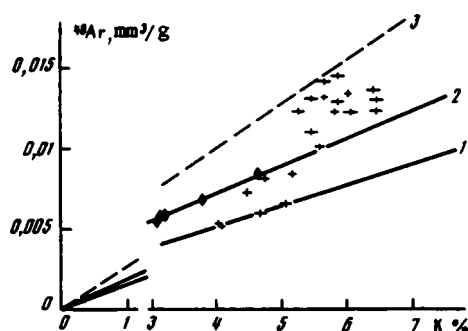


Fig. 1. $^{40}\text{Ar}_{\text{rad}}$ concentration as a function of potassium concentration for paleogenic glauconite fractions from Syria. Isochrons correspond to ages, million years: 1) 32; 2) 46 [4]; 3) 65. Sizes of crossmarks indicate values of analytic errors.

hydroxyl water itself. The maximum yield occurs at 300-400°C. Hydroxyl water can be partly lost not only in heating but also in glauconite trituration. However, according to experiments (Table 2) this involves no isotopic fractionation. The isotopic composition of hydrogen in Table 2 refers to water isolated at 1200°C after preliminary training of an unground specimen in a vacuum at 185°C for 5-6 hr (until a vacuum of $\sim 1 \times 10^{-5}$ mm Hg is reached).

The isotopic composition of oxygen and carbon was measured on a MI-1201V mass spectrometer; the isotopic composition of hydrogen was measured on a modernized GD-150 mass spectrometer. The values of $\delta^{18}\text{O}$ and δD are expressed in parts per thousand (‰) relative to the SMOW standard; $\delta^{13}\text{C}$ relative to PDB. The determination accuracies of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ were $\pm 0.2\text{‰}$; $\delta\text{D} \pm 3\text{‰}$. The method of preparation and analysis of glauconite specimens for K-Ar and Rb-Sr investigations have been described in [4].

DISCUSSION

A study of K-Ar and Rb-Sr systems of glauconites established two benchmark values of isotope age for the formation of biostratigraphic sediments based on planktonic foraminifers: 46 ± 1 million years for the base of the *Acarinina pentacamerata* zone (Lower Eocene) and 37 ± 1 million years for the base of the *Globigerapsis semiinvoluta* zone (Upper Eocene). The possibility of age interpretations of isotopic datings is based on several arguments. An important consideration is the convergence of ages calculated from K-Ar and Rb-Sr isochrons constructed from monomineral glauconite fractions [2, 4].

On the other hand, analysis of a considerable number of glauconite fractions isolated from glauconitic rocks of various stratigraphic levels of the Paleogene in Syria indicated

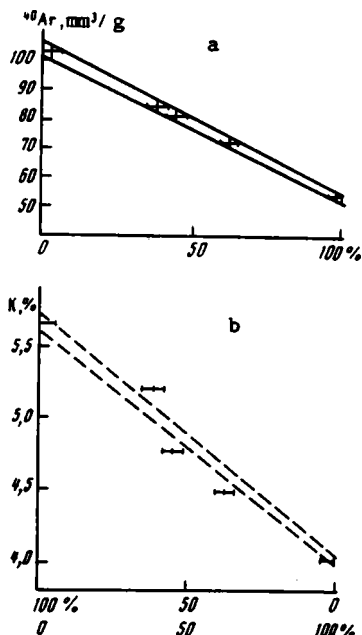


Fig. 2. Displacements of potassium and argon for glauconite fractions (specimen 17/83): a) specified displacement conditions according to $^{40}\text{Ar}_{\text{rad}}$ concentration; b) displacement hypothesis tested by potassium content in the same fractions. Correlation coefficient ($r = 0.9$) determines the plausibility of the hypothesis.

that converging K-Ar and Rb-Sr datings could not possibly be derived from them. All calculated (apparent) K-Ar "ages" were in the interval from the age of deposits of the given stratigraphic level (according to existing geochronological paleogenic scales - for example, [12, 21]) to 32-33 million years (Fig. 1).

For instance, Ar/K in the lightest density fraction of specimen 17/83 (*Globorotalia lehneri*, P12 zone, Middle Eocene) coincides with two earlier glauconite datings (specimens 836 and 717) of the same stratigraphic level from the Jebel-Abyad and Arak sections [8] and specimen 52/83 from the middle part of the *Orbulinoides beckmani* (P13) zone, the Middle Eocene of the section in wadi Harrar (Table 3), even though there are significant differences in potassium concentration (4.1-5.1%). For this reason, an explanation attributing the low argon-potassium ratios to random disruptions of isotopic systems of the mineral associated with the tendency in low-potassium glauconites for cation exchange (loss?) and a gradual loss of radiogenic argon is extremely doubtful [9].

The authors believe that an age on the order of 32 million years can determine the time of a certain geologic event that resulted in the formation of new K-Ar systems in glauconite fractions.

Let us assume that glauconite fractions (specimen 17/83) are represented by a mix of an "ancient" isotopic system corresponding to the sediment accumulation time (the maximum value of the ratio) and a "young" isotopic system (minimal ratio), which fixes a certain geologic event. If that is so, the intermediate potassium and argon concentrations would lie on the mixing line.

A test of this hypothesis (Fig. 2) confirms it fairly well and allows us to roughly estimate the age of sediments of the *Globorotalia lehneri* zone at 45 million years, which is just 5-7% older than the age calculated with Odin's scale [21]. The age based on the minimal ratio of 32 million years should then also have a geological meaning. The preceding arguments hold if both components of the mix are homogeneous.

Assuming that the divergence in isotopic datings has the same cause for all glauconites from the central Palmyras, we should expect that the distances of points on isochron planes are associated with a similar process of mixing of different-aged isotopic systems, which should affect both K-Ar and Rb-Sr ratios.

Thus, glauconite fractions of specimen 20/83 (Jebel-Hayan section, Lower Paleocene, *Globorotalia pseudobulloides* zone) exhibit younger apparent K-Ar and older model Rb-Sr ages as compared with what should be expected from the stratigraphic position of ~63 million years (Tables 4 and 5). The proportions of the "young" component (~32 million years) admixed to the "old" component (~63 million years) in glauconite samples 74, 75, and 76 (specimen 20/83) based on K-Ar ratios form the proportion 33:20:13 (Fig. 3). The corrections proportional to

TABLE 4. Potassium-Argon Systems of Density Fractions of Glaucinite (specimen 20/83)

Sample number	Density fraction, g/cm ³	K conc., %	Ar conc., mm ³ /g	Apparent age, million years
74	2.5-2.6	5.86	0.0123	53.3±1.8
75	2.6-2.7	6.05	0.0134	55.5±1.2
76	2.7-2.9	5.69	0.0132	58.5±1.0

TABLE 5. Rb-Sr Systems of Glaucinite Density Fractions (specimen 20/83)

Sample number	Material	Rb, mg/g	Sr, mg/g	⁸⁷ Rb/ ⁸⁶ Sr	⁸⁷ Sr/ ⁸⁶ Sr	Model age, million years
74	Glaucinite	177	57	9.019	0.7171	72.4
75	"	214	81	7.634	0.71496	65.8
76	"	198	198	2.885	0.71069	69.8
77	"	128	754	0.492	0.70837	-
78	"	84	1060	0.230	0.70798	-
20K	Carbonate	0	-	0	0.70783	-
20Φ	Phosphate	0	-	0	0.70780	-

these values to Rb-Sr characteristics of the specimens will probably "fit" their corresponding points upon the 63-million-year isochron.

This is indeed possible if we assume that the modern Rb-Sr systems of the specimens have inherited radiogenic strontium of a system homogeneous in ⁸⁷Rb/⁸⁶Sr accumulated during the ~30 million years that preceded the event; ~32 million years ago the system lost ⁸⁷Rb. As a result, the fractions of altered (i.e., "young" in terms of K-Ar ratios) parts of the globules in samples 74, 75, and 76 will be in the proportion 30:20:10, which is close to values estimated according to the K-Ar system. These estimates confirm that the alteration of glauconite systems occurred at a boundary of ~32 million years, i.e., in the Oligocene. About that time, the territory of Syria rose and emerged above sea level. Glaucinite alteration was obviously associated with penetration of meteoric waters into Paleogene sediments, as mentioned in [20].

We will attempt to estimate whether this event was reflected in the isotopic composition of oxygen and hydrogen of certain components of sedimentary rocks in the section.

δ¹⁸O and δD in Glaucinites. The isotopic composition of oceanic water is well known to be extremely homogeneous (δD = 0 ± 10⁰/‰, δ¹⁸O = 0 ± 1⁰/‰), and certainly it changed little during the entire Cenozoic. A simple method for determining the formation setting of glauconite from ancient sediments is by comparing it with glauconite or clay minerals of a similar composition from recent oceanic sediments. According to [24] δD in modern glauconite varies from -74 to -90⁰/‰ and δ¹⁸O from 21.8 to 26.3⁰/‰. In specimen 1040-2* of glauconite from the surface layer of Peruvian trench sediments, the following values were obtained: δ¹⁸O = 25.2⁰/‰. By and large, specimens from the Syrian Paleogene are comparable to modern glauconite both in isotopic composition of oxygen (δ¹⁸O from 20.9 to 23.8⁰/‰) and hydrogen (δD from -87 to 108⁰/‰) (Table 6). However, the variations of δD and δ¹⁸O are considerable and require an explanation. To begin with, we will estimate as accurately as possible the degree of isotopic fractionation in the glauconite-water system.

The scatter of isotope ratios in glauconite was attributed by the authors of [24] largely to exchange with isotopically light meteoric waters. Assuming that the isotopically heavy specimens are the least altered, they determine the fractionation coefficient α in glauconite-water systems (0.93 for hydrogen and 1.026 for oxygen). Similar values (0.94 and 1.027, respectively) have been obtained for montmorillonite. However, we cannot simply adopt these data, because the degree of isotopic fractionation is affected by chemical composition, which is intensely variable in glauconites.

The isotopic composition of hydrogen in hydroxy-containing minerals depends on the ratios of iron, magnesium, and aluminum ions in coordination [25]. High-aluminum minerals are en-

*This specimen is of zero K-Ar age.

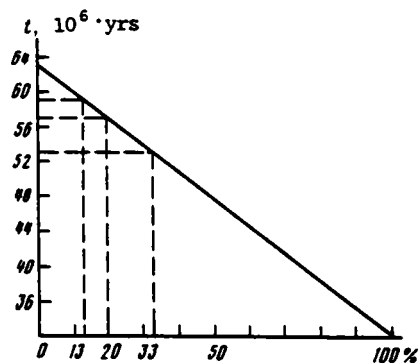


Fig. 3

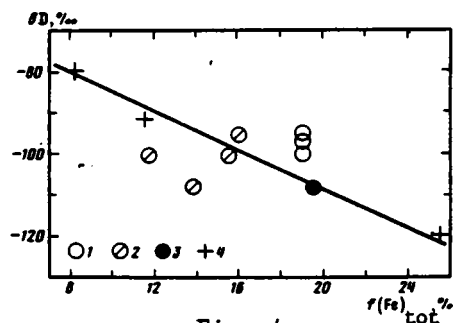


Fig. 4

Fig. 3. Evaluation of the proportion of "young" component in a mix of two K-Ar systems of fractions of specimen 20/83 with age ~62 and ~32 million years.

Fig. 4. δD vs. iron concentration in recent oceanic clay sediments and glauconite: 1) specimens with intact Rb-Sr and K systems; 2) specimens with intact Rb-Sr and K-systems from Syrian Paleogene rocks; 3) recent glauconite; 4) recent oceanic high-iron clay sediments.

riched in deuterium compared with minerals high in iron. In an equilibrium with seawater ($\delta D = 0$) at 10-15°C the value of δD in beidellite, kaolinite, margarite, and other minerals are close to -30‰ and nitronite to $100\text{--}110\text{‰}$ [14]. Recent high-iron clay sediments* exhibit a linear behavior of Fe_{tot} and δD (Fig. 4). Recent glauconite studied by us matches this relationship quite well.

The majority of Paleogene specimens from Syria also have a higher iron content (16-19%). The values of δD (from -87 to -100‰) correspond to an equilibrium with seawater. This means that glauconite during the postsedimentary period remained an isotopic system in hydrogen terms. The sole exception is specimen 20/83, which had the lowest ($< -100\text{‰}$) δD , with a low iron content (see Fig. 4).

The isotopic composition of oxygen generally does not indicate a significant hypergenic glauconite reworking. In the "classical" model, exchange with atmospheric waters is seen in direct correlation between $\delta^{18}O$ and δD . The specimens studied by us revealed no such correlation. They exhibited an inverse trend which likely reflected different formation temperatures (Fig. 5).

Although we do not have experimental calibrations of the relationship of isotopic fractionation between glauconite, water, and temperature, it is possible by analogy with other minerals (such as smectite from the Red Sea depression [15]) to estimate the temperature gradient $\delta^{18}O$ in glauconite as $\approx 0.2\text{‰}/T^{\circ}C$. Thus, if at 10°C in equilibrium with seawater the $\delta^{18}O$ of glauconite is $25\text{--}26\text{‰}$, then at 50°C it will be some 8‰ less.

Of the Syrian Paleogene glauconite specimens none has this low $\delta^{18}O$. Their maximum formation temperatures can be estimated at 25-30°C. It is possible that $\delta^{18}O$ in these specimens represents natural fluctuations of seawater temperature within 10°C.

Variations of $\delta^{18}O$ and δD in glauconite in principle can be attributed to another factor as well. During late diagenetic stages, when bottom water no longer penetrated the sediment, the composition of interstitial solutions may have been altered. Since clay minerals are enriched in ^{18}O and depleted of D compared with the water in equilibrium with which they are

*The following specimens of recent clay sediments have been analyzed (made available by V. I. Murav'ev and G. Yu. Butuzova): 1) station 980, depth 70-80, cm, Pacific aquatorium between Samoa and the Cook Islands, zeolites + nontronite $\delta D = -80$, $Fe = 8.35$; 2) station 1006, depth 160-170 cm, western slope of the Eastern Pacific Rise, 37° S, nontronite + ores, $\delta D = -92$, $Fe = 11.5$; 3) 1040-2, continental slope of Peru, glauconite (Table 6); 4) 1991, Red Sea, Atlantis II Deep, tetraferri-nontronite, $\delta D = -122$, $\delta^{18}O = 18.5$, $Fe = 26.0$.

TABLE 6. Isotopic Composition of Oxygen and Hydrogen in Paleogene Glaucanites

Specimen number	Age (zone)	Sample number	Density fraction, g/cm ³	$\delta^{18}\text{O}$, ‰ (SMOW)	δD , ‰	H ₂ O, %	Fe, %
59/83	P15	87	2,6-2,7	23,8	-95	4,7	19,0
		88	2,7-2,8	22,9	-	-	-
836	P12	-	2,45-2,7	23,1	-100	5,9	15,6
17/83	P12	69	<2,5	21,5	-90	5,1	-
35/83	P9	51	2,85-2,9	-	-100	3,5*	19,0**
		55	2,85-2,9	-	-97	2,9*	19,0**
		58	>2,9	-	-97	3,1*	-
		60	2,8-2,85	22,0	-97	4,8	-
21/83	P9	67	2,85-2,9	-	-96	2,5*	-
19/83	P9	94	>2,9	-	-96	2,2*	-
139/140	P4	122	2,7-2,8	23,3	-87	5,2	-
557	P2	-	2,55-2,6	22,3	-89	5,0	-
20/83	P1b	74	2,5-2,6	22,9	-95	4,5	15,9
		75	2,6-2,7	-	-108	4,6	-
		76	2,7-2,9	23,8	-100	4,7	11,7
		77	>2,9	-	-102	5,0	-
4820/16	P1c	-	2,55-2,6	22,2	-90	6,3	-
1040-2***	-	-	-	25,2	-108	5,0	19,5
GL-0****	-	-	-	-	-94	5,0	-

*Water concentration lowered because of phosphate admixture.

**Concentration calculated with adjustment for phosphate admixture.

***Recent continental slope in Peru.

****Odin's standard.

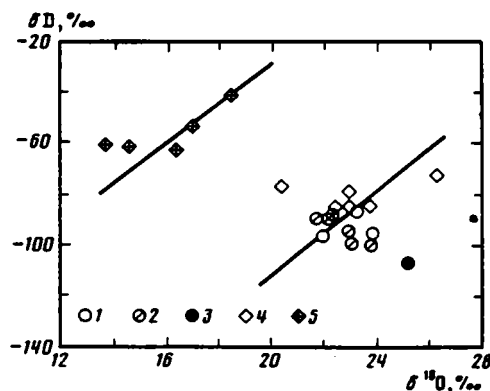


Fig. 5. Isotopic composition of oxygen in glauconite: 1) specimens with intact Rb-Sr- and K-Ar systems; 2) specimens with disrupted Rb-Sr and K-Ar systems from the Syrian Paleogene; 3) modern glauconite from continental slope of Peru; 4) Meso-Cenozoic glauconite [24]; 5) Precambrian glauconite [24]. Lines indicate the position of clay minerals, whose isotopic composition is equilibrated with atmospheric water.

formed, interstitial solutions become gradually enriched in D and depleted of ^{18}O . Accordingly, glauconite formed in the late stages of diagenesis can have lower $\delta^{18}\text{O}$ and higher $-\delta\text{D}$ as compared with glauconite formed in early diagenesis.

In terms of hydrogen, however, this effect is implemented only if the volume of neomorphous clay minerals is greater than that of interstitial solutions. This is unlikely.

TABLE 7. Isotopic Composition of Carbon and Oxygen of Cross Samples of Glauconite-Free Carbonates, Benthic Foraminifers, and Carbonate Matrix of Glauconite Horizons, ‰

Age		Zone	Plankton		Benthos		Matrix	
series	subseries		$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
Eocene	Upper	P17	0,1	26,3	0,0	25,8	-	-
		P16	-0,1	25,1	-	-	-	-
		P15	-1,3	24,4	-	-	-2,5	24,9
		P14	-0,3	23,5	-	-	-	-
		P13	0,0	24,4	-	-	-1,0	27,3
	Middle	P12	-0,3	23,9	-0,3	26,3	-	-
		P11	-0,9	26,0	-1,3	26,4	-	-
		P10	-0,3	24,8	-	-	-0,3	26,6
		P9	-1,7	25,4	-	-	-1,5	27,2
		P8	-2,4	24,8	-	-	-1,3	25,5
	Lower	P7	-1,2	24,5	-	-	-	-
		P6	-0,5	26,0	-	-	-	-
		P5	0,4	24,9	-	-	-	-
		P4	0,3	23,2	-	-	-	-
		P3	0,4	25,2	-	-	1,4	27,4
Paleocene	Upper	P2	-0,4	23,2	-	-	0,5	28,5
		P1c	0,0	26,1	-	-	-	-
		P1b	-0,1	25,6	-0,35	27,4	-	-
Maastrichtian	Lower	P1a	-0,1	24,6	0,0	26,4	0,4	27,9
		-	0,9	26,2	-	-	-	-

$\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in Carbonates. A large number of determinations of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ have been conducted on foraminiferal shells from deep-sea sediments in various parts of the world ocean [1, 13, 16, 22, 23]. These data are actively used in paleoclimatic studies and in stratigraphy. Variations of $\delta^{18}\text{O}$ are assumed to reflect mostly variations in water temperature. In planktonic foraminiferal shells from Upper Cretaceous-Eocene sediments, $\delta^{18}\text{O}$ varies from 28 to 31‰ (SMOW) and from -2 to +1‰ (PDB), which corresponds to temperature fluctuations approximately from 10 to 20°C.*

$\delta^{18}\text{O}$ in benthic and planktonic foraminifers varies more or less synchronously. $\delta^{18}\text{O}$ of benthos is higher by 1-2‰ than $\delta^{18}\text{O}$ in plankton (according to the normal temperature gradient between surface and bottom waters).

Variations of the isotopic composition of carbon in foraminiferal shells are mainly connected with the evolution of organic matter. The prevalent absorption of the light isotope ^{12}C by planktonic vegetable microorganisms during photosynthesis results in a relative depletion of carbon dioxide dissolved in water in this isotope; with virtually no isotopic fractionation carbon dioxide becomes bonded in shell carbonate [18]. Accordingly, the higher the biological productivity, the higher $\delta^{13}\text{C}$ in planktonic foraminiferal shells. The period of restructuring and a relatively lower biological productivity has occurred at the boundary between the Cretaceous and the Paleogene or between the Lower and Middle Eocene, corresponding to negative extrema of $\delta^{13}\text{C}$ [1, 19]. Generally, $\delta^{13}\text{C}$ of planktonic foraminifers rarely rises above 1-3‰. As to benthic foraminifers $\delta^{13}\text{C}$ in them usually is 1-2‰ lower than in plankton. This is due to the fact that, on the seafloor organic matter becomes disintegrated, and dissolved carbon dioxide is converted to ^{12}C . Carbon dioxide of an organic origin can be even more noticeable in the isotopic composition of diagenetic carbonates. The typical differences in isotopic composition between benthic and planktonic foraminifers (and forms inhabiting different depths) seem to disappear only in "critical" periods, for instance, at the boundary between the Cretaceous and the Paleogene [1].

Variations of the isotopic composition are an important element in isotopic stratigraphy and paleothermometry. Generally, such variations can occur both in subaerial and suboceanic environments. However, on land this is a much more real danger, because sediments are af-

*Isotopic oxygen temperatures are calculated from the formula given in [17]: $T^\circ\text{C} = 16.5 - 4.3 (\delta^{18}\text{O}_\text{C} - \delta^{18}\text{O}_\text{W}) + 0.14 (\delta^{18}\text{O}_\text{C} - \delta^{18}\text{O}_\text{W})$, where $\delta^{18}\text{O}_\text{C} - \delta^{18}\text{O}$ CaCO_3 (PDB), $\delta^{18}\text{O}_\text{W} - \delta^{18}\text{O}$ H_2O (SMOW). The melting of ice sheets on the earth has been estimated to lower $\delta^{18}\text{O}$ of the world ocean by 1‰; the value of $\delta^{18}\text{O}$ of the "Tertiary ocean" is assumed to be -1. In the modern ocean $\delta^{18}\text{O}$ is close to zero.

ected by atmospheric water, which is of a drastically different isotopic composition than seawater.

Table 7 and Fig. 6 present the results of determinations of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in Maastrichtian-Eocene carbonate rocks of Syria. First of all, one is struck by a stable shift of the isotopic composition of oxygen ($2-2.5\text{‰}$) in glauconitic horizons, as compared with glauconite-free layers. Possibly, it represents lower temperatures (by $8-10^\circ\text{C}$) at which the carbonate of glauconitic horizon was formed. In modern oceans this temperature difference is attained at depths of 500-1000 m [11]. Isotopic data thus suggest that the carbonate matrix of glauconite horizons is of a diagenetic origin.

The values of $\delta^{18}\text{O}$ in carbonate sediments of Syria are lower than in foraminifers from deep-sea sediments, which can be taken for the "norm." Calculations of paleotemperatures yield a range of $35-50^\circ\text{C}$ for carbonate rocks and $22-36^\circ\text{C}$ for glauconitic horizons ($\delta^{18}\text{O H}_2\text{O} = -1\text{‰}$) or at least $10-15^\circ\text{C}$ above the expected values. The distortion of paleotemperature information can in principle be due to the fact that Syrian carbonate rocks were formed in a slightly desalted basin (with salinity of 30‰).

Another possible cause of ^{18}O enrichment of carbonates could be hypergenetic interaction with meteoric waters. This could involve partial recrystallization of shells and also chemical (through solution) redeposition of calcite and filling of some cavities with calcite. Shells of benthic foraminifers are apparently replaced with secondary calcite. By oxygen isotopic composition they occupy an intermediate place between gross samples of organogenic limestones and the carbonates of glauconitic horizons. Glauconitic horizons that were more compactly cemented during diagenesis were probably rinsed by meteoric water less intensely than were loose glauconite-free horizons, and that could explain the difference between these two types in oxygen isotopic composition.

The conclusion of the diagenetic origin of the carbonate matrix of glauconitic horizons thus holds regardless of which alternative explanation we adopt. Making this final choice is difficult. On the one hand, the possibility of hypergenetic alteration of carbonates appears obvious, while, on the other, there are no grounds to assume that this alteration deleted all traces of information on a change of temperatures in the paleobasin, because the $\delta^{18}\text{O}$ curve generally repeats the curve of $\delta^{18}\text{O}$ variation in deep-sea Maastrichtian-Eocene sediments (see Fig. 6).

Let us assume that the intensity of hypergenetic alterations was about even in the entire bed, so that the possibility of estimating true temperature values but not their relative variations has been lost. Comparing the position of glauconitic horizons in the sections studied with the $\delta^{18}\text{O}$ curve, we see that they fall within a very narrow fluctuation interval of $\delta^{18}\text{O}$ from 24.9 to 25.4‰ (see Fig. 6). The accumulation of glauconite-rich sediments presumably occurred at a strictly specific ($\pm 1^\circ\text{C}$) temperature of the paleobasin, even though we cannot specify this temperature because of methodological limitations. The sole exceptions is glauconitic horizons from the P15 zone (*Globigerapsis seminvoluta*), for which the lowest $\delta^{13}\text{C}$ were obtained for the section, suggesting an enhanced contribution of carbon dioxide of an organic origin to carbonate formation. Higher seawater temperatures during accumulation of the P15 zone that were unfavorable for glauconite formation were probably compensated for by an active participation of organic matter in the diagenesis.

The variations of $\delta^{13}\text{C}$ in gross samples of Syrian carbonate rocks are quite consistent with global variations of $\delta^{13}\text{C}$ in deep-sea sediments. At the boundary of the Cretaceous and Paleogene and in the upper portions of the Lower Eocene, $\delta^{13}\text{C}$ decreases appreciably. The high biological productivity in the Upper Paleocene is reflected in a relatively high $\delta^{13}\text{C}$. We should also note that, compared with deep-sea sediments, carbonates from Syrian sections are depleted of ^{13}C by some 2‰ . There is no difference in the isotopic composition of carbon between gross samples and benthic foraminifers. This can hardly be explained by an effect of epigenetic solutions, especially since differences in terms of oxygen have been preserved in most specimens. Water geochemistry and circulation in this paleobasin were probably characterized by some peculiarities that have so far defied deciphering.

Glauconitic horizons in the upper strata are noticeably enriched in light carbon isotopes, which can naturally be associated with the normal alteration of high-organic sediment during diagenesis. In the lower portions of the section the ratios are opposite. The decay of organic matter associated with methane formation resulted in release of isotopically heavy carbon dioxide which under certain conditions could be fixed in diagenetic carbonates. Similar

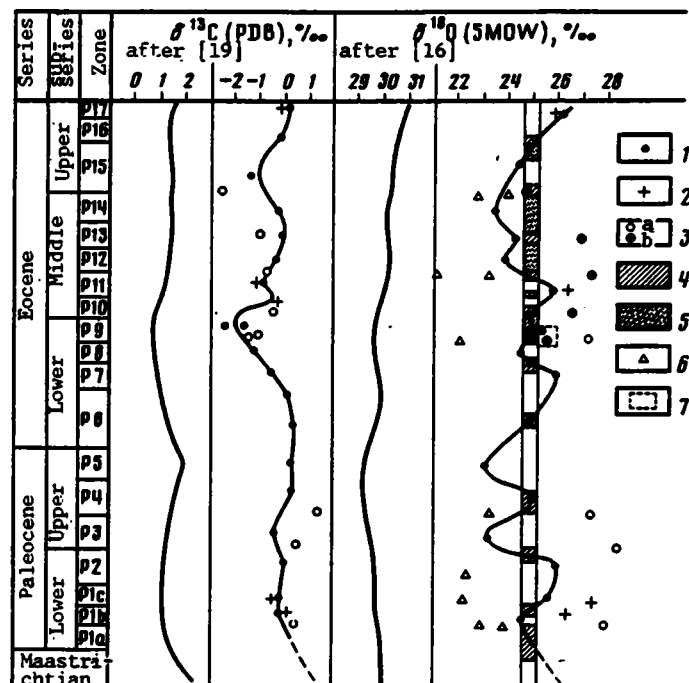


Fig. 6. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of carbonate and glauconite of the Maastrichtian-Eocene time. Relative length of zones based on planktonic foraminifers is given according to [11]: 1) glauconite-free carbonates (gross values); 2) benthic foraminifers; 3) carbonate matrix of glauconitic horizons of Jebel-Hayan (a) and wadi Harrar (b); 4) levels of glauconitic horizons in sections investigated; 5) same, in other sections on Syrian territory [5, 6]; 6) $\delta^{18}\text{O}$ in glauconite; 7) "anomalous" match of glauconite-free carbonates and matrix of glauconite horizon in the section of wadi Harrar.

processes could occur in that case as well; also, the effect is too small to state this with certainty.

In the present study we were confronted with two problems. First of all, we want to describe the formation settings of glauconite and glauconite-containing rocks on the basis of isotopic geochemical criteria. The other objective was to study the causes of variations in Rb-Sr and K-Ar-isotopic systems of glauconite. The results suggest that distortion of age data is caused by epigenetic effects that occurred at ~32 million years ago, rather than by rewashing or redeposition. The dating is geologically significant, because it corresponds to the time when the territory emerged above sea level in the Oligocene and could be associated with meteoric water penetration into Paleocene-Eocene rocks. The epigenetic processes clearly expressed in Rb-Sr and K-Ar systems of glauconites did not leave any comparably clear traces in the isotopic composition of oxygen and hydrogen. In most specimens it is close to isotopic equilibrium with seawater at temperatures not above 25-30°C, which corresponds to diagenetic conditions. An exchange with atmospheric waters is manifest in the isotopic composition of just one specimen (20/83), with disrupted Rb-Sr and K-Ar systems. This may be a reflection of the fact that the isotopic composition of epigenetic solutions (of a presumably atmospheric origin) in the subtropics did not deviate too much from the composition of seawater (by 30-40‰ in δD and 4-5‰ in $\delta^{18}\text{O}$). In northern areas the situation could be quite different.

Variations of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in carbonates of glauconite-free horizons of the Maastrichtian-Eocene rocks of Syria are generally synchronous to global variations of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ determined in deep-sea sediments. On the other hand, Syrian rocks are considerably depleted on ^{13}C and ^{18}O compared with "normal" sedimentary sediments, which can be caused both by the geochemical specifics of the paleobasin and epigenetic alterations.

There are reasons to assume that accumulation of glauconite-rich sediments occurred under quite specific ($\pm 1^\circ\text{C}$) paleobasin temperatures, although methodological limitations make it impossible to calculate the precise values. The formation temperatures of glauconite-containing carbonates were on average 10°C lower than for the surface rocks, which are determined by $\delta^{18}\text{O}$ of plankton. A series of facts indicates that the carbonate matrix of glauconitic horizons was formed during diagenesis. The carbonate component of the sediment was probably partly dissolved, reducing the thickness of the strata that contained glauconite horizons.

The diagenetic dissolution of biogenic carbonate sediments must have been associated with increased concentrations of mineral-forming elements (Si, Al, Fe, Mg, etc.) coprecipitated with biogenic sediments. These elements could provide initial matter for building the glauconite lattice and for several rare elements (such as iridium) brought to earth with cosmic dust. This sheds new light on the causes of stratigraphic disconformities at the Cretaceous-Paleogene and Middle-Upper Eocene boundaries and on the nature of geochemical anomalies during "critical" periods.

LITERATURE CITED

1. A. Boersma, "Paleotemperatures and ratios of carbon isotopes in a section from companion to the Paleocene and the boundary of the Cretaceous and the Tertiary in the Atlantic Ocean," in: *Catastrophes in the History of the Earth*, W. Berggren and J. van Kaufering (eds.) [Russian translation], Mir, Moscow, pp. 255-284 (1986).
2. V. I. Vinogradov, D. I. Golovin, and V. A. Krasheninnikov, "Isotopic dating by glauconite from *Globigerapsis seminvoluta* sedimentary zone (Upper Eocene) in the Eastern Mediterranean," *Dokl. Akad. Nauk SSSR*, **301**, No. 5, 1171-1174 (1988).
3. A. V. Peive and V. I. Vinogradov (eds.), *Geochemistry of Isotopes in Ophiolites from the Polar Urals* [in Russian], Nauka, Moscow (1983).
4. D. I. Golovin, M. I. Buyakaite, V. I. Vinogradov, and V. A. Krasheninnikov, "K-Ar and Rb-Sr dating of glauconite from the base of the *Acarinina pentacamerata* sedimentary zone (Middle Eocene) in the Eastern Mediterranean," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 7, 7, 75-81 (1986).
5. V. A. Krasheninnikov, "Zonal stratigraphy of the paleogene in the Eastern Mediterranean," *Tr. GIN Akad. Nauk SSSR*, Issue 133 (1985).
6. V. A. Krasheninnikov, V. I. Murav'ev, D. I. Golovin, et al., "Stratigraphy, lithology and glauconite horizons of paleogene sediments in the Palmyras (Syria)," *Vopr. Mikro-paleontologii*, Issue 29, 92-114 (1987).
7. I. V. Nikolaeva, *Minerals of the glauconite group in sedimentary formations* [in Russian], Nauka, Novosibirsk (1977).
8. V. A. Nikolaeva, I. V. Krasheninnikov, D. I. Golovin, and T. A. Ivanovskaya, "Possibilities of radiologic dating by glauconite of Paleogene sediments in the Eastern Mediterranean," *Litol. Polezn. Iskop.*, No. 5, 76-88 (1985).
9. I. V. Nikolaeva and V. N. Melenevskii, "Influence of ancient glauconite weathering on radiometric determinations," in: *Mineralogy and Geochemistry of Glauconite* [in Russian], Nauka, Novosibirsk, pp. 69-78 (1981).
10. V. P. Ponikarov, V. G. Kazmin, V. V. Kozlov, et al., *Geology and Mineral Resources of Foreign Nations. Issue 18: Syria* [in Russian], Nedra, Leningrad (1969).
11. R. Horn, *Sea Chemistry* [Russian translation], Mir, Moscow (1972).
12. W. A. Berggren, "Cenozoic time-scale: some implications for regional geology and paleobiogeography," *Lethaia*, **5**, 195-215 (1972).
13. A. Boersma and N. J. Shackleton, "Tertiary oxygen and carbon isotope stratigraphy, Site 357 (mid-latitude South Atlantic)," in: *Initial Reports of DSDP, U.S. Government Printing Office, Washington*, Vol. 39, pp. 911-924 (1977).
14. T. S. Bowers and H. P. Taylor, "An integrated chemical and stable isotope model of the origin of midocean ridge hot spring systems," *J. Geophys. Res.*, **90**, No. B-14, 12583-12606 (1986).
15. T. G. Cole, "Oxygen isotope geothermometry of smectites in the Atlantis II Deep, Red Sea," *Earth Planet. Sci. Lett.*, **66**, 166-176 (1983).
16. R. G. Douglas and S. M. Savin, "Oxygen and carbon isotope analyses of Tertiary and Cretaceous microfossils from Shatsky Rise and other sites in the North Pacific Ocean," *Initial Reports of DSDP, U.S. Government Printing Office, Washington*, Vol. 32, pp. 509-520 (1975).
17. S. Epstein, R. Buchsbaum, H. A. Lowenstan, and H. C. Urey, "Revised carbonate-water temperature scale," *Bull. Geol. Soc. Am.*, **62**, 417-426 (1953).

18. R. Kroopnic, R. F. Weiss, and H. Craig, "Total CO₂, ¹³C, and dissolved oxygen ¹⁸O at Geosecs II in the North Atlantic," *Earth Planet. Sci. Lett.*, 16, 103-110 (1972).
19. R. Letolle and M. Renard, "Evolution des teneurs en ¹³C des carbonates pelagiques aux limites Cretace (Tertiaire et Paleocene Eocene)," *C. R. Acad. Sci. Paris*, 290, 827-830 (1980).
20. J. P. Morton and L. E. Long, "Rb-Sr ages of glauconite recrystallization: dating times of regional emergence above sea level," *J. Sediment. Petrol.*, 54, No. 2, 495-506 (1984).
21. G. S. Odin, "The Phanerozoic time scale revised," *Episodes*, 1982, No. 3, 3-9 (1982).
22. I. Saito and J. van Douk, "Oxygen and carbon isotope measurements of Late Cretaceous and Early Tertiary foraminifers," *Micropaleontology*, 20, 152-177 (1974).
23. S. M. Savin, "The history of the earth's surface temperature during the past 100 million years," *Ann. Rev. Earth Planet. Sci.*, 5, 319-355 (1977).
24. S. M. Savin and S. Epstein, "The oxygen and hydrogen isotope geochemistry of clay minerals," *Geochim. Cosmochim. Acta*, 34, 25-42 (1970).
25. T. Suzouki and S. Epstein, "Hydrogen isotope fractionation between OH-bearing minerals and water," *Geochim. Cosmochim. Acta*, 40, 1229-1240 1976.

ASSOCIATION OF CHLORINE-CALCIUM SOLUTIONS WITH METASOMATIC DOLOMITIZATION OF LIMESTONE

V. G. Popov

UDC 553.776:552.543

With special reference to the Cis-Uralian region, the origin of chlorine-calcium brines is shown to be associated with the geochemical evolution of the waters of Late Paleozoic sedimentary paleobasins during the course of halogenesis and subsequent metamorphization of salt brine in the early stages of diagenesis and epigenesis. An analysis of lithologic and hydrochemical data and balance calculations in the brine-carbonate rock system indicated that the leading metamorphization process was dolomitization of Paleozoic and Upper Proterozoic limestones occurring under the influence of chloride magnesium brines of predominantly Permian evaporitic basins. The importance of this process for the physical and chemical conditions in the underground hydrosphere is emphasized.

Metamorphization of brines through dolomitization of limestone has been studied extensively by hydrogeochemists [1, 4, 7, 8, 10, 14, 15, 18, 20, 22], but the problem is still far from a final solution and is the subject of acute debate. One of the reasons for this is the limited volume of goal-oriented lithologic investigations and insufficient coordination of lithologic data with specific hydrogeochemical data. The gap between studies in the theory of lithogenesis and analysis of the formation process of the chemical composition of groundwater has had a negative effect on the development of these two fields of geology, as was rightly noted at the All-Union Conference on Groundwater and the Evolution of the Lithosphere [11].

It is no accident that special publications are usually concerned only with the qualitative aspects of postsedimentary alterations of carbonate sediments in their interactions with the liquid phase. Quantitative estimates of the mass transfer in brine-rock systems are extremely rare. Yet, studies in this area are needed both for understanding the genesis of brines, which are a valuable industrial resource, and for solving other problems in formation of oil, gas, ore, and other mineral deposits in the underground hydrosphere.

The present paper evaluates the role of postsedimentary dolomite formation processes in the development of chlorine-calcium (chloridic sodium-calcium and calcium-sodium) solutions, widespread in the deep portions of the sedimentary cover of ancient platforms [5, 6]. The study concentrated on the Cis-Ural region, which is a classical area of Paleozoic halogenesis in the eastern Russian Plate. Chemogenic sediments as indicators of brine-type paleobasins

Institute of Geology, Bashkirian Research Center, Ural Department, USSR Academy of Sciences, Ufa. Translated from *Litologiya i Poleznye Iskopaemye*, No. 4, pp. 97-103, July-August, 1989. Original article submitted June 6, 1988.

occur here at various stratigraphic levels (Frasnian and Famennian stages of the Upper Devonian; Visean and Moskovian stages of the Middle Carboniferous; and the Gzhelian stage of the Upper Carboniferous). However, halogenesis is especially widespread in the Early and (partly) Late Permian, when gypsum-halitic and sometimes carnolitic sedimentation were predominant. The thickness of Kungurian chemogenic rocks in the southern Cis-Uralian trough is up to 1-2 km; in Kazanian rocks, in the central part of the Nuzuluk depression, it is 0.2 km.

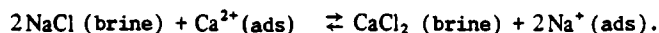
Chloridic brines associated genetically with Permian halogen formations are represented by three main geochemical types: 1) magnesium, sodium-magnesium (230-400 g/L) intrasalt solutions which are the product of concentration of salt-bearing mother brines prior to halite-carnalite halogenesis stages; 2) sodium (36-320 g/L) above- and under-salt solutions formed as a result of interaction of infiltrational waters with the solid (mainly halitic) phase of halogenesis; and 3) sodium-calcium and calcium-sodium (200-330 g/L) subsalt brines predominant in the region's sedimentary strata.

Chlorine-calcium brines form a spatially consistent hydrochemical zone, up to 2-3 km and more in thickness, associated with Carboniferous, Devonian, and Late Proterozoic (Vendian and Riphean) sediments that occur in a quasistagnant hydrogeodynamic setting. They are characterized by a high metamorphization (rNa/rCl 0.1-0.7, $CaCl_2$ to 50-80%), low sulfate content (rSO_4 100/ rCl 0.02-0.7), high bromine content (to 2.2 g/liter, Cl/Br 70-160), high concentrations of potassium (to 2.4 g/liter) and rare elements, acid reaction (pH 5.9-7.0), negative redox potential (Eh to -300 mV), and nitrogen-methane and methane gas composition with a heightened potassium content.

The formation mechanism of such brines has not been deciphered as of yet. Several hypotheses have been suggested: endogenous (juvenile), infiltrogenic, and sedimentogenic-diagenetic (lithogenetic) theories. Each has its exponents and detractors among hydrogeologists and hydrogeochemists investigating the Volga-Ural region.

It has been determined that in the Cis-Ural region the endogeneous factor does not exercise a regional influence on the formation of these waters. This is indicated, among other things, by studies of the isotopic composition of helium in fluids of the sedimentary cover in the eastern Russian Plate [12].

There is a common view that chlorine-calcium brines evolve through lixiviation of rock salt by infiltrogenic water (or diffusional transfer of sodium chloride from Permian halogenic rocks) followed by exchange-adsorptional processes between the resulting sodium chloride brines and terrigenous rocks according to the Geodroits scheme:



However, our experimental studies [13] have demonstrated that, as terrigenous sediments subside from the hypergenesis zone into the catagenesis zone and become compactified and lithified, the exchange and adsorption capacities of the rocks are greatly reduced. The capacity of an adsorbed complex at a depth greater than 1-1.5 km is at most 5-10 mg eq/100 g, which is determined both by structural and mineralogic characteristics of the clay fraction (mainly hydromica and chlorite) and by physicochemical settings of the catagenesis zone (high temperatures and pressure, acid environment, etc.).

According to our estimates of the hydrogeochemical effect of cation exchange in deep Paleozoic horizons of the Cis-Ural region, the sodium chloride brine cannot be metamorphosed by ion exchange to more than 5% of calcium and yield $rNa/rCl < 0.96$.

Therefore, exchange in adsorption had a minor role in forming the chlorine-calcium brines of the region, especially considering the limited occurrence of terrigenous rocks in the Paleozoic and an extremely low adsorptive capacity of carbonate sediments, which make up as much of 90% of the Paleozoic section.

The entirety of facts appears to fit best with the lithogenetic concept, which attributes the formation of chlorine-calcium brines to geochemical evolution of waters of sedimentary basins of the past geological epochs during the course of halogenesis and subsequent metamorphization of halogenic brine during di- and epigenesis. An analysis of lithologic and hydrogeochemical settings of the Cis-Ural region indicated that the leading role among metamorphization processes belongs to dolomitization of Paleozoic and Late Proterozoic carbonate sediments that occurred during descending migration of chloridic magnesium mother brines through these sediments, mainly from Permian evaporitic paleobasins.

The sinking of heavy (a density of 1.3-1.4 g/cm³) brines from halogenic basins, and the brines squeezed out of halogenic rocks as these were lithified, into an environment of lower-salt waters under the effect of geogravitational factors is confirmed by: 1) ubiquitous occurrence in subsalt strata of brines of halogenic paleobasins and their derivatives; 2) high recent infiltration rates of brines from industrial effluent storage to subjacent strata (tens of meters per year in the Cis-Ural region); and 3) experimental studies by Valyashko, Polivanova, and Zherebtsova [2] on the mechanisms of transport of brines with different specific weights.

These investigators determined that the process is close to isochoric and occurs without significant change of volume with a limited mixing of solutions. The densities of relatively low-salt waters flowing in upward jets are eventually associated with the surface halogenic basin, where they take part in subsequent salt-forming processes.

Metasomatic dolomitization of limestones belongs to the group of exchange and absorption phenomena. According to Smirnov [17], it is implemented on a scale of geological time in a natural environment because it occurs through an intradiffusional mechanism. A thermodynamic and kinetic analysis by Krainov et al. [7] indicated that the intensity of dolomitization increases with degree of mineralization, temperature, and rMg/rCa of the brines. The investigators also determined that dolomitization is a more complex process than a simple exchange according to Marignac's scheme: $2CaCO_3 + MgCl_2 = CaCO_3 \cdot MgCO_3 + CaCl_2$. It passes through subsequent stages with formation of magnesium-containing calcite, protodolomite, and dolomites variously enriched in calcite. Importantly, the substitution of calcium of the solid phase by magnesium from the brine, resulting in calcium accumulation in the chloride solution, has been proved experimentally [4, 22].

A number of publications have acknowledged the existence of a genetic relationship between chlorine-calcium brines and dolomitization of carbonate rocks [1, 4, 7, 8, 14, 18, 20-22]. On the other hand, some investigators, while noting the advantages of the process in energy terms, believe this course of formation of chlorine-calcium solutions problematic, if at all possible. One of the main considerations mentioned is the limited occurrence of secondary (dia- and epigenetic) dolomites in sedimentary basins. The authors often cite Strakhov [18], who said that brines should not be used to explain the origins of heavily dolomitized rocks.

In this context, it is important to discuss the types of dolomite rocks and their occurrence in the sedimentary basin of the Cis-Ural region. Syundyukov [19] identified three main genetic types of dolomite: sedimentary, diagenetic, and epigenetic. The first type includes stratal dolomites, which occur over a wide territory. It is characterized by a pelitomorphic or fine-granular texture, and absence of any noticeable traces of metasomatism of calcite by dolomite, and other features typical of primary chemogenic dolomites. These are dolomites found in the Namurian and Upper Visean stages of the Lower Carboniferous, in the Kashirian-Podolsk horizon of the Middle Carboniferous, and the Kungurian stage of the Lower Permian.

Diagenetic dolomites are found amid limestones as separate lenses, stocks, and bed-shaped bodies, sometimes stretching for tens of kilometers. Dolomites of this type exhibit clear traces of secondary alteration: metasomatic substitution of calcite by dolomite, strong variability of dolomitization within a body, etc. This type includes dolomites of the Upper Devonian-Tournaisian complex, the upper part of the Middle Carboniferous (Machkov horizon of Shkapovo, Tuimazy, Sergeevka, Chermasan, and other areas), the Upper Carboniferous (Tuimazy, Chekmagush, Kashkul, Arpan, Tatyshly, and other areas), and the Sakmar stage (Tuimazy, Ishimbai, and other areas). Diagenetic dolomites are also predominant (50-150 m) in the Lower Famennian substage of the Devonian that occurs almost everywhere in the Cis-Ural territory.

A correlation is observed between the degree of dolomitization and the structural-genetic specifics of limestones and the presence of clay admixtures and their infiltrational properties [3, 19]. Pelitomorphic and fine crystalline limestones experienced the most dolomitization. The dolomitization of coarse crystalline and organogenic limestones is less frequent and usually uneven. The selective dolomitization of limestones appears to reflect the fact that pelitomorphic and fine crystalline calcite has a higher surface energy than does the coarse crystalline variety.

Limestones of a pure composition are much more dolomitized than are clay limestones. Vishnyakov [3] attributes this to the different capillarity (permeability) of these limestone

TABLE 1. Thickness of Metasomatic Dolomites in the Cis-Uralian Paleozoic Section, m

Stratigraphic subdivision	Oil exploration area							
	Tui-mazy	Shka-povo	Serge-evka	Chek-magush	Arlak	Taty-shly	Ishim-bai	Voskre-senka
P ₁ k	38	34	17	34	30	61	22	-
P ₁ a	-	10	31	10	2	8	13	-
P ₁ as-s	37	21	-	19	10	14	140	3
C ₃	52	14	5	33	35	72	5	-
C ₂	141	57	48	43	19	56	50	29
C ₁ sr	23	36	51	42	27	23	43	55
C ₁ ok	26	17	-	26	12	39	30	50
C ₁ tl	12	-	-	-	-	-	-	-
C ₁ t	18	3	5	6	19	-	7	-
D ₃ -fm	51	9	-	-	18	21	7	-
D ₃ fr	-	9	-	-	8	21	14	11
D ₂ g	-	-	-	-	-	-	4	-
D ₂ e	-	2	-	-	-	-	7	-

varieties. This effect is beyond doubt, because the capillaries are the paths through which magnesium brines penetrate limestone sediments. However, clay particles themselves must play an important role, because they envelop calcite grains and prevent, or at least inhibit, dolomitization.

Dolomites formed by epigenetic processes are also widespread in the carbonate strata of the Paleozoic rocks in the Cis-Ural. They are found as veinlets and veins cutting across the enclosing rocks, filling cavities and pores between grains, making up crustlets, sec. This means that dolomites of this type were formed in a preexisting rock with rigid bonds.

An intermediate position in terms of metasomatism (between diagenetic and epigenetic dolomites) is occupied by so-called dolomitization pseudobreccias, which are found throughout the Paleozoic carbonate section. The advanced degree of dolomitization, its selectivity, and the substitution of dolomite for fine pelitomorphous calcite bring pseudobreccias close to diagenetic dolomites, but the association with cracks indicates that dolomitization evolved in an already lithified sediment, as is typical for epigenetic dolomites.

Secondary dolomites are widespread in the Upper Proterozoic as well as the Paleozoic. According to Morozov, Ivanova, and Andreev [9], Lower Riphean dolomites with a thickness of up to 1.5 km are exclusively metasomatic in the eastern Russian Plate.

The foregoing data confirm the widespread occurrence of dolomitization processes in the sedimentary strata of the Cis-Ural region. This is due primarily to paleohydrogeochemical environments during the Permian epoch. Because of an exceptionally high concentration of magnesium in mother brines (rMg/rCa up to 150-200 with a salt glauconite of 230-400 g/L and more) they have an extremely high dolomitization potential.

We will estimate quantitatively the role of dolomitization processes in the development of chlorine-calcium brines.

The total thickness of dolomitized rocks in various stratigraphic subdivisions of the Paleozoic in the region varies from single-digit to tens of meters, sometimes up to 140 m. The overall thickness in profiles of well in oil prospecting areas ranges from 157 to 398 m (see Table 1), i.e., 5-27% of the Paleozoic thickness. Magnesium content in pure (chemogenic) dolomite is 13.2%. In carbonate sediments of the Cis-Ural Paleozoic, according to Ronov [16], it varies from 1 to 10% (an average of 5%). The weight of dolomitized rocks, 300 m thick, with a density of 2.8 tons/m³ on an area of 100,000 km² is mDR = 300 m · 10¹¹ m² · 2.8 tons/m³ = 8.4 · 10¹³ tons. The amount of magnesium in them is mMg = 8.4 · 10¹³ m · 0.05 = 4.2 · 10¹² tons.

Since metasomatic substitution of limestone calcium solutions by magnesium occurs in equivalent amounts and the atomic weight of calcium is 1.6 times that of magnesium, the amount of calcium brought into the liquid phase will be slightly larger than this estimate.

Chlorine-calcium solutions in the Cis-Ural region are found at a depth of 250-700 m (an average of 500 m). Calcium concentration in them, which corresponds to calcium chloride, increases with depth from 1 to 55 g/liter. Within various structures in the region the type of calcium accumulation in brines has its specific features associated with the hydrodynamic

conditions of rocks enclosing the brines. In the depth interval of 500-1000 m it amounts to ~10 g/liter, at 1000-1500 m to 15 g/liter, and at 1500-2500 m (the bottom of the Paleozoic section) to 30 g/liter. The average calcium content in brines of Paleozoic strata, up to 2000 m, is assumed to be 25 g/liter.

The average calcium concentration in Vendian-Riphean brines, adjusted for available analytic data and the specifics of vertical hydrogeochemical zonality, is 40 g/liter. The total sediment thickness ranges from 0 to 8500 m, with an average of 4000 m.

The volume of chlorine-calcium solutions in the 2-km Paleozoic rock thickness with porosity of 5% on an area of 100,000 km² is estimated at 10⁴ km³ (2 km · 100,000 km² · 0.05); the amount of calcium in them is 2.5 × 10¹¹ tons (10¹³ m³ × 25 kg/m³).

The volume of brines in Vendian-Riphean rocks is 2 × 10⁴ km³ (4 km × 100,000 km² × 0.05). The total calcium content in these brines is 8 × 10¹¹ ton (2 × 10¹³ m³ × 40 kg/m³).

Thus, the amount of calcium released from carbonate rocks in Cis-Ural Paleozoic during metasomatic processes (5 × 10¹² ton) is more than enough to form chlorine-calcium brines of the appropriate composition not only in Paleozoic but also in Late Proterozoic sediments (total calcium is 10¹² ton). The existing calcium disbalance is to some extent due to infiltration processes during the hydrogeological stage that followed brine formation, when chloride sodium-calcium brines were pressed out of the top portions of the sedimentary cover in the basin.

An important fact is that migration of magnesium solutions from Permian basins into subjacent sedimentary complexes in all likelihood was started long before formation of the salt-bearing bed. Subsequently, accumulation of halogenous rocks was associated with their compactification and reduced porosity (from 40-50 to 2% and less). As a result, immense masses of chlorine-magnesium brines were pressed out and sank by gravity into deeper parts of the sedimentary basin.

According to experimental data [2], extrusion of intracrystalline brine into subjacent rocks occurs at a thickness of accumulated salt less than 200 m. As halogenesis continues, the hydrodynamic communication between the upper and lower parts of the bed and the halogenic basin breaks off.

Additional magnesium brine sources could be the self-precipitated entities in the Carboniferous and Devonian basins mentioned earlier. Metasomatic dolomitization in the brine-carbonate rock was not a single-act process, as assumed in calculations by Strakhov [18]. It was a multistage evolution which supported the development of considerable masses of secondary dolomites and chlorine-calcium brines associated with them.

In basins with halogenous formations, the geochemical consequences of dolomitization were not limited to development of metasomatic dolomite and sodium-calcium brines. Studies by Bogashova, Goleva, Krainov, and Kholodov et al. indicate that rocks release into the solution not only calcium but geochemically related strontium and barium and some ore elements (zinc, copper, and lead) in quantities sufficient for development of stratiform deposits. In particular, in interstitial solutions of the Krasnokamsk salt deposit in the Cis-Ural region the concentrations of lead, zinc, and copper are 10, 2, and 8 mg/kg. High concentrations of heavy metals in interstitial brines in areas of ancient halogenesis are now viewed as a regular result of their evolution in sedimentary rocks. By contrast, in interphase magnesium-for-calcium exchange, boron is extracted from the mother brine, which accumulates in metasomatic dolomites as low-solubility calcium borates [13].

Another important fact is that epigenetic dolomitization also results in an increased porosity of carbonate rocks (by 10-12%), i.e., formation of secondary oil, gas, and ground-water collectors. This emphasizes the important influence of metasomatic processes in carbonate strata on the physicochemical conditions of the underground hydrosphere.

LITERATURE CITED

1. E. A. Baskov, "Main features of occurrence and formation of the basic types of underground brines in the Siberian Platform," in: Underground Brines of the USSR [in Russian], VSEGEI, Leningrad, pp. 61-75 (1976).
2. M. G. Valyashko, A. I. Polivanova, and I. K. Zherebtsova, "Experimental study of movements of brines with various specific weights in porous rocks in connection with vertical hydrochemical zonality," *Geokhimiya*, No. 3, 312-316 (1963).

3. S. G. Vishnyakov, "Genetic types of dolomite rocks in the northwestern margin on the Russian Platform," Types of Dolomite Rocks and Their Genesis [in Russian], Izd-vo Akad. Nauk SSSR, Moscow (1956), pp. 109-255.
4. N. K. Vlasova and M. G. Valyashko, "An experimental study of the genesis of chlorine-calcium waters," in: Proceedings of a Seminar on the Formation of Chloridic Calcium-Sodium Waters [in Russian], VSEGINGEO, Moscow (1968), pp. 121-125.
5. I. K. Zaitsev, Hydrochemistry of the USSR [in Russian], Nedra, Leningrad (1986).
6. V. A. Kiryukhin and N. I. Tolstikhin, Regional Hydrogeology [in Russian], Nedra, Moscow (1987).
7. S. R. Krainov, E. V. Dobrovol'skii, L. I. Matveeva, et al., "Geochemical analysis of groundwater capacity for dolomite formation in sedimentary basins," Geokhimiya, No. 9, 1285-1302 (1986).
8. V. I. Lebedev, "Sedimentary and diagenetic theory of chlorite-calcium water formation," Vestn. Leningr. Gos. Univ., No. 6, 26-40 (1966).
9. S. G. Morozov, T. V. Ivanova, and Yu. V. Andreev, "Chemical composition and genesis of sedimentary Upper Proterozoic rocks in the eastern Russian Plate," in: Geochemistry of Platform and Geosynclinal Sedimentary Rocks and Ores [in Russian], Nauka, Moscow (1983), pp. 40-48.
10. E. V. Pinneker, Problems of Regional Hydrogeology [in Russian], Nauka, Moscow (1977).
11. Groundwater and Evolution of the Lithosphere [in Russian], Vol. 1 Nauka, Moscow (1985).
12. B. G. Polyak, I. N. Tolstikhin, and V. P. Yakutseni, "Isotopic composition of helium and heat flux: geochemical and geophysical aspects of tectogenesis," Geotektonika, No. 5, 3-23 (1979).
13. V. G. Popov, "Formation of mineral-bearing groundwaters in the Cis-Ural region," Doctoral Dissertation, Geological-Mineralogic Sciences, Leningrad State Univ. (1987).
14. V. D. Poroshin, "Formation of high-salt chlorine-calcium brines," Litol. Polezn. Iskop., No. 9, 55-61 (1981).
15. E. V. Posokhov, Formation of Chloridic Waters in the Hydrosphere [in Russian], Gidrometeoizdat, Leningrad (1977).
16. A. B. Ronov, "Chemical composition and formation setting of Paleozoic carbonate strata of the Russian Platform (based on lithologic and geochemical maps)," in: Types of Dolomite Rocks and Their Genesis [in Russian], Izd-vo Akad. Nauk SSSR, Moscow (1956), pp. 256-343.
17. S. I. Smirnov, Origins of Salinity of Groundwater in Sedimentary Basins [in Russian], Nedra, Moscow (1979).
18. N. M. Strakhov, Development of Lithogenetic Ideas in Russian [in Russian], Nauka, Moscow (1971).
19. A. Z. Syundyukov, Lithology, Facies, and Oil and Gas Prospects of Carbonate Sediments in Western Bashkiria [in Russian], Nauka, Moscow (1975).
20. A. E. Khod'kov, "Formation of groundwaters of a sedimentary origin," Tr. Vsesoyuz. Nauch.-Issled. Inst. Galurgin, Issue 35, 452-470 (1959).
21. V. N. Kholodov, "Types of catagenesis and sedimentary-hydrothermal ore formation," in: Groundwaters and Evolution of the Lithosphere, [in Russian], Vol. 1 Nauka, Moscow (1985), pp. 226-253.
22. A. A. Shebesta, "A study of the interaction of groundwater with rocks at high temperatures (with special reference to extraction of geothermal energy)," Candidate's Dissertation, Geological-Mineralogical Sciences, LGI, Leningrad (1985).

This paper discusses applications of mathematics in sedimentology. Some recommendations given in reference books are criticized. The deficiency of the overall composition, distortions in lists of concepts, and various specific errors are noted.

In 1983 a reference book on lithology was published as a handbook intended for broad groups of Soviet lithologists [11]. In 1984, a monograph was published as an introduction to a course in modern theoretical geology [10]. Both books contain chapters on the application of mathematics in modern sedimentology (and lithology) authored by S. I. Romanovskii. Since these books appeared, the present reviewer has been requested on various occasions by several individuals to publish a review of the mathematical presentation in these book because the respective chapters contained statements that contradicted authoritative publications. Such a review was written in 1986 and was concerned solely with the mathematical sections of [10, 11]. A discussion of the review with editors suggested that the original text should be supplemented with an explanation of some of the concepts, which the author assumed to be self-evident. The result is this revised version of the 1986 review.

ON SOME GENERAL CONCEPTS

In the past decades the science of sedimentary rocks, termed *lithology* in Russian literature, began to be called *sedimentology* in foreign publications. The root of the term "sedimentology" was not clear to Russian readers. For some reason it was associated with "sedimentation," and the science was interpreted as the study of the deposition of sediments. In reality, the root here is the noun "sediment," and sedimentology is precisely the science known as lithology in Soviet literature. It is desirable to make terminology as international as possible; however, the term "lithology" in English language literature is a synonym of the term "material composition," i.e., it is used there as was suggested in the past century. One can write, for example, of the lithology of a section consisting of gneisses and cut across by dikes. This is confirmed by the definition of sedimentology in the Russian translation of an American geological dictionary [12]. In the present paper, the terms "lithology" and "sedimentology" are used as synonyms.

We will explain some mathematical concepts used in the books under review. They will be illustrated by a simple example. All the sands of the delta of the Neva are referred to as a population (or "general population" in the expanded form of the term). It is obvious that the sands of the entire population have a certain average granulometric size. This average size cannot be actually determined because it is impossible to measure all the grains. The average size is a nonrandom quantity which is referred to as an expectation. All such nonrandom quantities are called the parameters of the population. The notion of a population does not include the definition of relationships of the grains of sand depending on their spatial position. However, if we make a polished section of a sand block, we can study the relationships of the relative positions of grains - for instance, along the horizontal hair in the field of a microscope. Such a sequence of grain positions along a hair is called the realization of a random or stochastic process. Random processes are classified by various features. Subsequently, we will consider a random process known as the Markovian chain. It is a process where, for instance, the probability of occurrence of a grain of a fixed mineral composition in the crosshairs of a microscope depends on a limited number of grains of a fixed composition situated before that grain (moving in the direction in which the grains are counted). If the probability of occurrence of a grain of a given composition in the cross-

Institute of the Geology and Geochronology of the Precambrian, Academy of Sciences of the USSR, Leningrad. Translated from *Litologiya i Poleznye Iskopaemye*, No. 4, pp. 104-116, July-August, 1989. Original article submitted August 5, 1986.

hairs depends only on the preceding grain, such a random process is referred to as a simple Markovian chain. If it depends on n preceding grains, it is a Markovian chain of n th order. For brevity, in situations where one wants to emphasize the specifics of Markovian relations, one says that the analysis is made in "Markovian terms."

Either for a population or for a process it is impossible to determine the exact values of parameters. But, taking a limited number of specimens, we can measure an analogue of a parameter from selected specimens. The specimens thus selected are referred to as a sample; the values of the parameters determined from a sample are called "parameter estimates" or their "statistics."

It should also be mentioned that the word matrix refers to a square table filled with numbers. Such tables can be manipulated in the same way as numbers arithmetic to solve all kinds of lithological problems.

These basic concepts are insufficient for work with specific objects, but they are helpful for analysis of the books under review. A detailed presentation of the material can be found in Russian and English editions of the book [4].

A HISTORY OF THE PROBLEM

The introduction of mathematics to geology can be divided into two periods. The first began at the turn of the century and continued until the Second World War. It was limited to attempts at applications of elementary statistics with descriptive purposes. The second stage was introduced in 1944 and is still continuing. It involves research and development of optimal methods for solution of geological problems by mathematical tools and their application in geological practice. The first period can be viewed as one of preliminary evolution. The second period is one of maturity of the scientific discipline of mathematical geology.

Applications of mathematics in the first and the second periods were largely aimed at solving lithologic (sedimentologic) problems. The International Society for Mathematical Geology, founded in 1968, was subsequently closely associated with the International Association of Sedimentologists. As a result, lithology became the geologic discipline where mathematicians could realize the potential of mathematics in geology to the fullest extent. Non-trivial solutions of lithologic problems by mathematical methods, development of profound conceptual models, and specific problems and their solutions in mathematical applications made it reasonable to combine the work in lithology on the basis of mathematics into a special section of lithology: mathematical sedimentology. This idea was proposed at the Ninth International Sedimentological Congress in Nice [21] and published in the USSR [3]. Subsequently, programs of international sedimentologic congresses included a section for mathematical sedimentology [19]. Such was the brief history of the development of mathematical methods in lithology as far as the organizational aspect is concerned. We will list the main scientific results that were achieved.

1. The notion that sedimentary formations are realizations of (mathematically) random phenomena was fully justified. This idea, which followed from years of research by Vernadskii, and constituted the basis of all studies in 1944, made it possible to develop the methodological aspect of these studies.

2. A general methodological procedure has been found for solving lithological problems by mathematical means. On this basis it was possible to develop the general theory of lithogenesis in modern terms with exact estimates. Lithological problems were solved in terms of conceptual stochastic modelling. The basic possibility of this approach and especially the construction of particular models were not self-evident, but resulted from a rephrasing of lithology in mathematical terms. It was necessary to master a specific mathematical apparatus as dictated by the lithologic problems. Neither mathematicians nor lithologists could have accomplished this if acting on their own.

3. Ideas of the theory of random processes, which now form the foundation of mathematical sedimentology, are extremely valuable and promising for creation of models.

4. Two problems occupy a special place in terms of the depth of ideas and the specific tools used. One is reevaluation of the phenomenon of cyclicity [18, 23]. It becomes increasingly clear that in most instances notions of cyclicity must be replaced by a concept of a random process with recovery. The importance of transition to these new concepts is obvious, but the time when this will occur is determined by the development of a new paradigm. The second problem is one of the balance of sedimentary matter on the earth's surface and its

migration and loss as a result of subduction of lithospheric plates under the continents [15]. While for the former problem the tools of solution have been developed and the end-result is clear, the latter is a large-scale problem that requires considerable effort for an exact formulation. Another problem should also be mentioned which involves the relationship between accumulation and erosion during the course of formation of the planet's sedimentary cover. It was posed by us in early 1948 in terms of local sections; in 1949 Kolmogorov solved it in principle. At present, on the basis of a restatement of the problem in Markovian terms, it can be formulated on a global scale [20].

By 1976, the above results were reported in a monograph [18]. Unfortunately, the section on mathematical methods in lithology in [11], despite its claim of covering materials up to 1981, does not contain these results.

We now proceed to a discussion of the mathematical chapters of the two above-cited books.

NOTES ON A HANDBOOK OF LITHOLOGY

The section of [11] reviewed here consists of four chapters (chapters 39-42). They are reviewed separately, with a general summary. Chapter 39 is entitled "Problems of Lithology Solved With Mathematical Methods and Electronic Computers." The author rightly notes that mathematics in lithology can be used at two levels: a) for descriptive purposes to obtain succinct characterizations of material, and b) for constructing models of lithologic processes. One cannot but agree with the author's statement that all the formulations could be programmed for a computer. These general statements have often been repeated (and often presented much more substantively than in the chapter under review) and are certainly true.

Chapter 40 is concerned with elementary statistical techniques for processing of empiric data. The title of the first section indicates that it deals with distribution of discrete quantities and their statistical characteristics. The second section describes the methods of statistical testing of hypotheses.

The title of the first section is misleading: it does not correspond to its contents. Romanovskii describes a method of constructing a density histogram of a continuous random quantity reduced to a discrete form. This well-known technique is useful in certain situations, especially in manual calculations. However, it is irrelevant to the question as to whether the random quantity studied is discrete or continuous. In the closing paragraph, the author mentions that an empiric distribution carries full information about the random quantity studied. (The word "random" is omitted by Romanovskii in this section, although it is essential for correct understanding.) This statement is generally untenable; it applies only to independent random quantities studied by simple sampling. Lithologists should exercise caution in using this distribution.

Giving formulas for moment characteristics, [11] does not mention that they are provided for calculation of estimates of these characteristics.

The relationship between estimates and characteristics (parameters) of distributions is the subject of a separate discipline: mathematical statistics. This distinction has far-reaching implications. Estimates of parameters as such are of no interest for a lithologist. They provide merely a starting point for making judgments concerning parameter values. This important principle is overlooked by the author. In addition, there are several omissions in this section. A reference book is expected to use commonly accepted notation. For instance, the standard deviation (a parameter) is commonly denoted by σ and its estimate by S . Yet, in the text, the estimate is denoted by σ , which can confuse readers using this reference book as a guide to especial literature. Granulometric investigations are expressed in an uneven scale of particle sizes. Different scales correspond to different sets of sieves. Calculations for granulometric analysis are conditional, and, therefore, S values for different sieve sets can vary. For this reason, quantile characteristics are appropriate in studies of sedimentary granulometry. They are less sensitive to inequality of orders than moment characteristics. The author mentions that, in practice, lithologists often deal with asymmetric distributions. The causes of asymmetry in this case should be clarified, because it can occur for technical reasons, particularly with a faulty sampling scheme.

The second section of this chapter has a mysterious title: "Methods of Statistical Testing of Hypotheses." Like the first section, it is concerned with elementary techniques of statistical processing. A perusal of this section indicates that the author attempted to present here an extremely complex field of mathematical statistics, known as the method

of testing of statistical hypotheses. This brilliant accomplishment of human thought has provided a profound foundation for several modern disciplines. Let us see how the author tests hypotheses statistically. This is explained in the first sentence. The author claims that "testing of hypotheses in statistics is understood as a comparison of sample characteristics by means of special criteria" [11, p. 483]. Since the presentation presumably applies to ordinary situations, let us try to understand what this may refer to. It is clarified by the following example. Suppose that we take from a conglomerate layer 100 pebbles and from another conglomerate layer 200 pebbles and measure their roundness; the mean roundness for the pebbles from the first layer will be $\bar{x}_1$ and from the second layer $\bar{x}_2$. It turns out that it is insufficient to take these two numbers to determine which of the sets of pebbles has a better mean roundness. Special criteria must be introduced. What kind of criteria can be provided in this case? According to Romanovskii's statement, we are dealing with existing samples. Thus, there is no randomness and no need for criteria. Yet, the author suggests that they are necessary and that the problem should be solved (in this case) by using Student's t-test. This reference makes it clear that the author has in mind not with the mean values of samples (as he states) but in fact expectations a_1 and a_2 of the roundness degrees of pebbles in layers 1 and 2, respectively, and that he wishes to estimate the expectations from the means of samples. He must then describe the procedure of pebble sampling so as to be able to estimate a_1 and a_2 . If we know some additional details, we can evaluate our values of the mean roundness of all pebbles in layers 1 and 2 of these conglomerates. With this formulation, we have a problem and a hypothesis as to the relationship between a_1 and a_2 ; it is obvious that some additional knowledge is necessary for solving this problem [4]. The author then gives an example with a pair of samples and an attempt at estimating the difference between them in terms of Student's test. This is erroneous. The problem of paired comparisons is not equivalent to the problem of simultaneous comparison of all pairs. Comparison of pairs is the purview of variance analysis, and Student's formula cited by the author does not apply here. It also makes no sense to give formulas (Student's and Fisher's tests) without explaining the situations where they can be used. In fact, they are applicable only to statistically independent observations on normally distributed quantities; in addition, for Student's test some constraints on variances are imposed. Applications of Student's test have been described in detail in the geological literature with special reference to specific material [22].

Chapter 41 is concerned with methods of multidimensional statistics used in lithologic studies. It begins with the following statement: "Ease and accessibility of processing of large files of empiric data at the present time makes it possible to derive from an initially small number of lithologic characteristics a practically unlimited number of derivative features, requiring a deep understanding of the essence of the mathematical methods used, because it affects the statement of problems and interpretation of results," [11, p. 484]. In the preceding analysis we followed this apt advice and will abide by it in the rest of this review.

With regard to this chapter, we should note that the results of correlational, regression, dispersional, and discriminant analysis require no additional explanations if the analysis is done on normally distributed quantities characterized by simple sampling [4]. This principle, although omitted in this reference book, should always be borne in mind. The second fact, mentioned by us earlier (also overlooked in the book), is that estimates of population as such are meaningless. They are needed to verify hypotheses concerning the characteristics of objects (which are assumed to be homogeneous). The section on correlation analysis omits to mention a fact extremely important for lithologists, namely that r is a measure of linear relationship and its value is between +1 and -1. Nor does it state that two random quantities can be connected by a nonlinear functional relation but that the correlation coefficient between them even in that case can be equal to zero. The author does not note that the value of r calculated from observed data is a random quantity used to estimate the true (parametric) correlation coefficient of the population studied. He does not state that r and its absolute value are a direct indicator of an existence of a linear relationship only in theoretical models. The value of r calculated with formula (10) can be arbitrarily close to unity, but this does not prove that the quantities studied are indeed characterized by a linear statistical correlation. For verifying this assumption, one must have the estimate r and know the combined distribution functions X and Y and the number of observation pairs n used in calculations. One must also bear in mind that in practice it is extremely difficult to ensure a representative sampling. If the sampling conditions are violated, no theoretical estimates of "significance" can be relied upon. It is more practical to estimate significance

r from approximate formulas, as is done in monograph [8]. One should also consider the possibility of false correlations, where a lithologist operates with a closed system of calculations (such as percentages or grams per metric ton). Regrettably, these practically important facts are not mentioned in the book. These are elementary facts about linear correlations that a lithologist has to know before undertaking independent calculations. Thus, in sum, this section does not really describe correlation analysis.

The section on correlation should be followed by a section describing linear regression and analyzing the regression model often used in lithology. This analysis should be provided for the one-dimensional case, because it provides easier explanation of the fundamental ideas of these methods. The techniques of the one-dimensional case can then be easily transferred to multidimensional situations. Unfortunately, this extremely important section is missing from the book.

After correlation analysis, Romanovskii dedicates two sections to popularize the work, of a certain member of the staff of the All-Union Geological Institute. We will return to this at the end of this review. We now proceed to the section on multiple linear regression. The language of the very first sentence in this section is dramatically different from the language of the preceding text. It is precise and clear, but the presentation is divorced from lithology and uses terms that have not been explained either before or here. In the preceding text, Romanovskii tried to explain most elementary concepts to lithologists. Yet, in this section, without any warning, he begins to use complex specialized terminology. For instance, already in the second line, "conditional mean values" are mentioned.

If a lithologist, in Romanovskii's opinion, is at a level where the meaning of a histogram or an arithmetic mean needs to be explained, it stands to reason that the conditionality of means requires to be defined. There is also confused usage of special terms. For instance, the author writes that the purpose of regression analysis is to estimate "linear regression in terms of the general model" [11, p. 486]. One gets the impression that this refers to calculations on a plane. However, a regression surface is not necessarily a plane, and general models are inapplicable. The sentence would be meaningful if we assumed that it refers to regression in the framework of a general linear model rather than linear regression in terms of a general model. If that is so, the author should have clearly specified the entity with respect to which the model is linear. If my assumption is correct, it is confusion similar to that in the presentation of the testing of statistical models. Mathematics speaks in precise terms, and reshuffling adjectives in this way is unacceptable.

Next, follows technical derivations and calculation of estimates of regression coefficients. It is doubtful that a lithologist needs to know these techniques. Especially baffling is the fact that all these derivations are formulated in matrix terminology. The author thus begins to use the language of linear algebra, while still addressing readers for whom he earlier deemed it necessary to explain the concept of an arithmetic mean. We should note also that, editorially, the matrix F in formula (11) should be preferably presented in a version that does not require the transposition sign. An inexperienced reader would then have an expression without superfluous notations (the transposition sign), the use of this sign requires an explanation, again omitted by the author. Comments to (11) also must be edited. Z and E should be put in parentheses. According to the author, the subsequent text gives a description of the standard procedure of the least squares method. One can only guess why this may be necessary. Be this as it may, from expression (11) in the case of the least squares method in its standard form we obtain $FF^TB = FZ$, rather formula (12) given in the book. What D means, how D can be explained in terms of $\hat{D}$, which is not explained either, and why some of the matrices and vectors must be put in parentheses remains a mystery even for a reader who has used the method described in the book for years. The obscure description of the general linear model made it necessary to introduce a special section on trend analysis. Had expression (11) been explained clearly, the section on trend analysis would be an inherent component of the section on regression models. As to the description of trend analysis, the main concept is missing: the author does not say when it should be applied (when the results are nontrivial) and what the considerations are which determine the order of a polynomial (or the number of harmonics) in constructing the surface of a trend. The latter question has been discussed with lucidity in a monograph by Romanova [8], cited by the author. In lithological constructions it is essentially different from the simple problem of approximation. As elsewhere, this part contains obvious errors. The distinction between conditional coordinates of points and simple coordinates will remain unclear to the lithologist. The author then quotes a representation of a trend from Romanova's book. However, in formula

(13) from [11] he provides an expression for an exponential, not a polynomial, trend. Generally, in formula (13), an arbitrary integer n rather than 3, where $n = 3$, can be written (this case is a reflection of the specifics of the problem at hand). One is utterly confused by the statement that approximation to a trend surface by means of a step-by-step regression procedure is necessarily not polynomial. If the term step-by-step regression procedure is taken in the usual mathematical sense (i.e., approximation with progressively higher degrees of the variable), then why approximation in terms of, say, Chebyshev's polynomials is not polynomial? As the end of the section on trends, the author again provides some minute details of computational procedures. Since they are utterly superfluous in a book of this kind, I did not check these formulas.

Variance analysis is presented in an extremely limited version, even though it has been conducted in lithological studies on many occasions on the basis of a linear model that offers a vast variety of methods [7, 17, 24]. The presentation begins with an example that is bound to jar a lithologist. On page 489, the author speaks of classification according to facies and stratigraphic characteristics, while at the end of the same page he speaks of rocks. This implies that he equates facies and rock, even though this very book includes a special section discussing the concept of facies. One would wish for more accuracy also in the definition of the objectives of variance analysis. Its purpose is to study how mean content of a random quantity (for instance, the content of a heavy fraction) is affected by various combinations of factors. The chapter ends with factor and discriminant analysis. Factor analysis, especially in the form of the method of principal components without statistical estimates (i.e., in its purely algebraic form) has gained undeserved popularity in all geological sciences, including lithology. The reason is the naivete of investigators who believe that the name of this type of analysis has the same meaning as the respective term in lithology. Mesmerized by etymology, these investigators adopt uncritically any results obtained with the method of principal components and interpret them in substantive terms. Yet, there is an abyss between the actual meaning of numbers yielded by the analysis of principal components and the results produced by a computer — a gap that neither lithologists nor other geologists have attempted to bridge. The point of the matter is that Romanovskii omitted to mention something that we have emphasized earlier: the value of mathematical applications in lithology is that they offer a total for rejecting certain theoretical constructs of lithologists. In other words, a theoretical construct in lithology can ultimately be rejected by a mathematical technique (provided the construct is expressed in a form lending itself to mathematical analysis). The problem is raised in comparison of mean values and is extended to variance analysis if one is limited to the set of questions discussed in the book. The problem of discriminant analysis discussed in this book is also representable in this form. The situation is different with the method of principal components (or factor analysis in general). Without lithological argumentation, it is assumed that in the system coordinates taken for study of the object (such as the content of bromine and other chemical elements in sylvinite, the thickness of a layer in a sylvinite horizon, and the distance of a test point from the surface), the frames of reference were selected so that they blur the natural relationships. In order to clarify these relationships, one has to represent observations in an orthogonal coordinate system. This makes observations mutually independent, and can produce two results. Either observations in an orthogonal system of coordinates will be reduced to a single group, or they will form two or more groups representable on a plane in the orthogonal coordinate system.

If observations are not divided into groups but placed together, they are assumed to be generated by a single "factor." If analysis reveals that observations produce several groups, the assumption is that they were generated by several "factors." Such unconditional, straightforward, and naive interpretations can produce serious errors. Lithologists should be cautioned about this pitfall. The popularity of the method of principal components is a reflection of a failure to understand what mathematics can give to lithology and a naive belief that the method always "works," i.e., that it always produces numbers that can be interpreted. The question is, what does this "work" actually yield? There is no direct answer, because there is no basis for a direct interpretation of the numbers. The author discusses two procedures that involve factors analysis. What units are adopted to measure the distance in the space of features in the generalized sense? If this measurement is expressed in values of the cosine of the angle between points (this value is expressed by the correlation coefficient), one speaks of procedure R. If the distance between the points is expressed in a linear measure (as the Euclidean distance), it is the procedure Q. There are no complications, and linear algebra has nothing to do with this distinction. Romanovskii rightly does

not introduce the concept of linear algebra into the book at this level i.e., he recognizes here that something undertaken three pages earlier and then repeated in the section on discriminant functions one page later is improper. In conclusion, I will note that factor analysis provides a solution if the number of the features of factors studied is smaller than the number of observations. Otherwise, its results are uninterpretable. This is an important reservation, especially since publications that make precisely this error sometimes appear even in the *Doklady Akademii Nauk SSSR*.

The final section of this chapter deals with discriminant analysis. As in all the other cases, there is no discussion of special analysis. The author merely attempts to explain the meaning of a discriminant function and its applications. He describes how a hyperplane can be calculated when a discriminant function is used for classification purposes, as is usual in geology. The true objective of discriminant analysis is different: the purpose is to place a single sample in a specified population, ensuring minimal diagnostic error.

Before completing the review of chapter 41, we should note that the author mentions the equality of covariance matrices and the Anderson-Bakhadur procedure in calculations of discriminant function. He notes that in practical terms the inequality of covariance matrices can be neglected. Some 15 years ago geologists, relying on the word of mathematicians rather than actual study of the subject matter, decoded that discriminant analysis is inapplicable without special procedures if covariance matrices of populations are unequal. For some time this property of discriminant analysis was mentioned in geological publications. Yet, as far as this reviewer knows, none of the authors who declared this limitation ever explained why discriminant functions could not be calculated in this case. Actually, the situation is simple. Mathematically, discriminant analysis begins with a capability for evaluating optimally classification errors. This involves a comparison of covariance matrices and resolution of problems raised by the inequality of these matrices. However, geologists who used discriminant functions ignored classification errors. Calculations were reduced to determining the position of a hyperplane that divided a set into two populations and enabled a sample to be placed in one or the other. No classification (diagnostic) errors were estimated. Geologists have never provided an experimental confirmation of the possibility of ignoring the inequality of covariance matrices. In fact, they implemented a method that was simpler in practice than in theory and was satisfactory as a first approximation.

The closing chapter of the mathematical section in the book is concerned with Spearman's ranked correlation coefficient. An attentive reader will be baffled by the presence of this chapter, which is not justified by the preceding presentation and is superfluous. A reading of the chapter shows that the author tried to offer a simpler method for calculating a correlation estimate than a usual correlation coefficient, declared to be an extremely precise estimate of the degree of relationship. This statement is meaningless. Both coefficients can be exact if the sample is built correctly, the object is suitable for study (the conditions are identical), and the number of observations is sufficiently large. However, recalling that the ordinary correlation coefficient is closely related to the logical theory of regression analysis, we understand how much information an investigator will lose if he calculates the ranked correlation coefficient instead of it. For instance, the book includes a chart in Fig. 39.1 showing that ranked correlation coefficient and usual correlation coefficient are indistinguishable. Yet, if we are limited to ranked correlation coefficients, we are unable to test whether the data used to plot Fig. 39.1 are suitable for estimating the degree of connection. On the other hand, if we calculate the correlation coefficient and determine the deviation of observations from the coordinate line, we will see immediately that observations are generally dependent; in this case the data should not be mixed and the general correlation coefficient should not be calculated. In this case, one ought to compute correlation coefficients separately for each group of specimens and then compare the resulting correlation coefficients, as was explained to lithologists more than three decades ago [2]. Generally, in this age of microcomputers there is little sense in recommending the abacus and nomograms.

Generally, ranked correlation coefficients are useful in certain specific situations, but in statistics there are many methods more useful and important for lithology than this coefficient. One is remained, for instance, of the elegant, simple, and flexible tool: conjugation tables, especially those constructed on the basis of information measures. The theory of tolerant limits is valuable for the study of small samples. One can also mention the popular cluster analysis, etc. All these methods are absent from the book. Descriptions of a secondary procedure occupies more than a quarter of this part. Finally, this material

ought to be at least edited properly. We have already given an example illustrated by Fig. 39.1. Concerning this example [11, p. 495] we read, "calculation of Spearman's coordination coefficient"; however, Spearman never proposed this coefficient, and the reader is completely at sea in understanding what it means and why it has been introduced. There are many other failings of this kind.

The chapter ends with a list of references. One questions the purpose of this list. If it included readings for lithologists on issues discussed in this part of the book, one would only welcome it, but of the six publications (selected from thousands of papers with mathematical applications in lithology) the list gives three studies on ranked correlation. The first of these is, in essence a instruction for manual calculations, which is repetitive and of no general interest. Of the remaining three, two have never been reviewed and almost never quoted. Why would they be instructive to a lithologist?

As mentioned earlier, the section covers methods created at the All-Union Geological Institute (Burkov's correlation of correlation). These methods have been repeatedly criticized in publications as unsuitable. The book gives no new information on this score. Analyzing these defective recommendations would be a waste of the reader's time.

PRESENTATION OF LITHOLOGICAL PROBLEMS THAT REQUIRE MATHEMATICAL MODELING

So far we have discussed only the presentation of mathematical problems [11]. We will now consider lithological problems that are mentioned in [10] and [11] without use of mathematics and are unclear. The authors of the mathematical chapters in the two books did not present these problems in a properly constructive form. This refers, above all, to chapter 6 of the reference book and chapter 4 of monograph [10]. The material discussed in these chapters is concerned with the variation of the composition of layers in vertical sedimentary section. The authors of [11], on the basis of a general paper by N. B. Vassoevich and V. V. Menner, propose names for external characteristics observed in various portions of the section and identified unequivocally. It remains unclear of what use to lithology and what solutions can be derived if we accept these terms for description of sections. Similar questions are discussed in [10]. Unlike [11], Romanovskii suggests classifying "dynamic types of sedimentary cycles" [10]. Those who have studied sections in situ will agree that reconstructing the dynamics of sedimentation is an extremely complex endeavor. Once the dynamics of sedimentation has been reconstructed, classifying is easy. On the other hand, if a classification of regimes is developed in general terms rather than on the basis of specific material, there are no guarantees that the sedimentation dynamics could be reconstructed from such data. No alternative for the solution of the classification problem is offered either in the reference book or in the monograph. Yet, there is such an alternative. It has been discussed in numerous publications, and many workers now believe that it is the main road for lithology in this area. Authoritative scientists, primarily Slutskii, Khinchin, Kolmogorov, and Feller, in the middle of this century developed the above-mentioned theory of random processes. According to this theory, first introduced into geology by this writer back in 1949 [1] and later used by numerous investigators, a sedimentary profile is interpreted as a realization (a "sample" in the terms explained at the beginning of this review) of a random process. As mentioned, the random process depends on time, so that its characteristics are a function of time only on the average. In a specific expression, such as a profile studied by a lithologist (a sample), the characteristics at any point of the section can vary in a broad range and take different values with different probabilities. From this point of view, the important aspect of a profile is its general structure, while specific variations of composition and their local relationships may be of no import. This leads to the problem of isolating a structure of the process, which can be solved by conceptually modeling. Classifying the specific manifestations of a process in a specific realization serves no purpose. The fundamental works by Vassoevich and Menner and the "dynamic settings" of Romanovskii are no more than a tribute to an obsolete tradition, which holds no future for lithology. The new approach, adopted in numerous publications, have already yielded practical results and cannot be ignored. With regard to the methodology suggested by this writer (i.e., stochastic modeling) Romanovskii has commented twice. In 1977 he wrote: "the model of sulfate sedimentation ... has been developed by A. B. Vistelius jointly with O. V. Sarmanov ... The original statement of the problem and an elegant method of deriving the distribution function ... can be recommended as a paragon of flawless analysis of a geological phenomenon" [9, p. 79]. Further, he writes: "We have dwelled on Markovian models in the first part of the book [9, p. 72]. A brilliant example of implementation of this method is the monograph by A. B. Vistelius" [9, p. 368].

In 1984 Romanovskii again discusses the issue in this monograph [10]. Here, he criticizes my interpretation of these methods (we should note that this is the conventional interpretation accepted by such authorities as Kolmogorov, and others). I am also accused of an unjustified restriction of the main goal of mathematical geology, advertisement of a worthless work by a Donetsk geologist, E. A. Yakovtsev [14], and popularization of an efficient method for modeling the layer formation process. Romanovskii's statements of 1977 and 1984 refer to the same publications and the same ideas. In the interval between these two dates, the method of this reviewer was discussed in a special publication at an international level [25] and was acknowledged to be highly promising. In 1984, at the 27th international Geological Congress, it was the object of discussions in several sessions. It was recognized as the leading method of world mathematical geology. It is unclear what Romanovskii proposes in place of this method. What is the reader supposed to believe? Romanovskii's statements in [9] or [10]?

The accusation that this reviewer has restricted the definition of the main purpose of mathematical geology hardly deserves discussion. It was the reviewer in [4] who provided a precise definition of mathematical geology; no other definition has been given since.

Finally, objections to Markovian models [14]. Any random sequence has its corresponding Markovian matrix. This is trivial when the matrices are individual and carry valuable information. Each random sequence is not a realization of a Markovian model, especially a model that generates a Markovian chain of second order. Apparently, Romanovskii fails to understand that we operate with models, while he discusses matrices, i.e., a different concept. In [6] Romanovskii gave clear evidence of his failure to understand this issue. He stated directly [6, p. 146] that any sequence of layers has a Markovian matrix. Romanovskii drew the faulty conclusion that any Markovian matrix corresponds to the same Markovian sequence. This is wrong, and discussions based on this assumption are irrelevant.

Returning to Markovian concepts, our techniques yielded nontrivial and valuable results. Yakovtsev has demonstrated that a sequence of layers is an analogue of Markov's homogeneous chain. The number of states on which the chain is specified includes coal. This leads to a direct practical conclusion: deposits that have not yet been uncovered by wells between sections studied by Yakovtsev should include areas promising for industrial coal reserves. When we approach the boundary of this area, the section will lose the properties discovered by Yakovtsev. Yakovtsev pointed out several other potential applications ignored by Romanovskii.

In a difficult search for ways of understanding the structure of sedimentary strata, we have completed the hardest stretch of the road. Random processes with recovery turned out to be provide a foundation for real headway in this important area of geology. This progress can be hampered only by extraneous causes.

It is important to fill a gap in the handbook and to recommend literature on mathematics in lithology (sedimentology). These are publications that will help lithologists to understand the essence of the problem statement, employ constructively statistical techniques, and clarify the specifics in statements of problems: monograph [18] will familiarize a lithologist with the general approach and the specifics of problem statement; monograph [8] gives examples of practical application of the methods that Romanovskii attempted to describe in [11]; studies [4, 13, 15, 20] offer a broad view of the questions that can be solved by conceptual stochastic modeling; a detailed example of a model that leads to a process with recovery can be found in [23]; finally, [4, 5, 13, 16, 20] give modern statements of the problem and describe conceptual paleogeography in terms of terrigenous components.

LITERATURE CITED

1. A. B. Vistelius, "On layer formation mechanisms," Dokl. Akad. Nauk SSSR, 65, 191-194 (1949).
2. A. B. Vistelius, "Study of relationships in mineralogy and petrography," Zap. Vsesoyuz. Mineral. o-va, No. 1, 58-73 (1956).
3. A. B. Vistelius, "The environment of lithogenesis and the fundamental problem of mathematics in sedimentology," in: Papers Presented by Soviet Geologists at the Ninth Sedimentation Congress on the Problems of Modern Lithology and Sedimentary Mineral Resources [in Russian], Nauka, Novosibirsk, pp. 185-189 (1977).
4. A. B. Vistelius, Principles of Mathematical Geology [in Russian], Nauka, Leningrad (1980).

5. A. B. Vistelius, M. E. Demina, and B. P. Kharlamov, "Fundamental problem of exploratory geochemistry and paleogeography in terms of terrigenous components as a problem of random field structure," in: Geological Information and Mathematical Geology [in Russian], Nedra, Moscow (1976), pp. 37-47.
6. A. A. Trofimuk (ed.), Methodology of Lithologic Studies [in Russian], Nauka, Leningrad (1985), pp. 138-146.
7. M. F. Mokhnach, "Influence of factors on average bromine concentrations in developed beds of Verkhnekamsk potash salt deposit," Geokhimiya, No. 8, 1223-1235 (1979).
8. M. A. Romanova, Recent Sand Sediments in Central Karakum [in Russian], Nauka, Leningrad (1971).
9. S. I. Romanova, Recent Sand Sediments in Central Karakum [in Russian], Nauka, Leningrad (1971).
10. New Ideas in Theoretical Geology [in Russian], Nedra, Leningrad (1984).
11. N. B. Vassoevich, V. I. Librosvich, N. V. Logvinenko, and V. I. Marchenko (eds.), A Handbook of Lithology [in Russian], Nedra, Moscow (1984).
12. An Explanatory Dictionary of English Geological Terms [in Russian], Mir, Moscow (1979).
13. B. P. Kharlamov, "A mathematical model of accessory mineral accumulation in sedimentary deposits," in: Studies in Mathematical Geology [in Russian], Nauka, Leningrad (1978), pp. 80-90.
14. A. E. Yakovtsev, "Alternation of lithologic rocks types in sections of the Carboniferous in Donets basin," Ugol' Ukrainy, No. 7, 47-49 (1975).
15. M. F. Dacey and A. Lerman, "Sediment growth and aging as Markov chains," J. Geol., 91, 574-590 (1983).
16. B. K. Lee and H. E. Jobson, "Stochastic analysis of particle movement over a dune bed," Prof. Paper 1040, U. S. Geol. Surv., Government Printing Office, Washington (1977).
17. M. A. Romanova, "Checking linear hypotheses in factor evaluation by use of trend-surface gradients in the investigation of eolian deposits," J. Internat. Assoc. Math. Geol., 2, 231-341 (1970).
18. W. Schwarzacher, Sedimentation Models and Quantitative Stratigraphy, Elsevier, New York (1975).
19. Sediments, Sediments Down-Under, 12th Internat. Sediment. Cong., First Circular (1984).
20. R. Thompson, "A stochastic model of sedimentation," J. Internat. Assoc. Math. Geol., 8, 753-779 (1984).
21. A. B. Vistelius, "The main problems of mathematics in sedimentology," in: 11th Congr. Internat. de Sediment., Theme III, Nice, pp. 107-112 (1975).
22. A. B. Vistelius, "Mathematical geology and the progress of geological sciences," J. Geol., 84, 629-653 (1976).
23. A. B. Vistelius, Gravitation Stratification: Future Trends in Geomathematics, Pion Press, London (1981), pp. 141-177.
24. A. B. Vistelius and M. E. Demina, "Variations of some heavy minerals in recent beach sands," J. Internat. Assoc. Math. Geol., 14, 159-185 (1984).
25. E. H. T. Whitten, "Vistelius's views on conceptual stochastic models," J. Geol., 85, 326-331 (1977).

METHODOLOGY OF RADIOGRAPHIC INVESTIGATIONS INTO THE STRUCTURE OF SUBAQUEOUS SEDIMENTS

V. M. Voskoboinikov and B. I. Krakovskii

UDC 549.08:551.35

In this article, we will discuss the physical properties, geometric conditions, and methodology associated with radiographic studies of sediment textures, composition, and moisture. The textures of muds of various origins are characterized.

The use of traditional techniques and methods of studying textural features of near-shore marine and deep-water sediments of natural composition and moisture is accompanied by a number of objective difficulties due to the high degree of "sensitivity" of the sediments to mechanical influences leading to the disruption or deformation of textural elements. This situation complicates textural analysis to a significant degree and frequently distorts its results.

In practice, the study of the structure of recent sediments includes three levels of investigation at present in contrast to the micro- and meso-levels of investigation, the macro-level is usually thought of as including visual description of the object without the use of any technical instrumentation. Such an approach results in a subjectivization of the information obtained and completely excludes the possibility of a quantitative evaluation of ground structure. The most significant complications arise during the visual description of macrotextures of clay sediments. The seeming homogeneity of muds, especially in the moist state, not only thwarts discovery of the complete spectrum of textures but also leads to erroneous conclusions with respect to the absence or limited occurrence of textures.

Significant progress toward solving the above-mentioned problems is afforded by the use of the method of x-ray radiography, based on the penetrating ability of x-rays and the subsequent recording of the weakened x-ray beam by means of special photoemulsions [5].

During the passage of an homogeneous beam of x-rays of a specific wavelength through a material, the intensity of the beam will decrease, as a consequence of absorption of the radiation, in a manner proportional to the attenuation coefficient μ , which is independent upon the nature of the absorbing material [6]:

$$I_x = I_0 e^{-\mu x}, \quad (1)$$

where I_0 is the intensity of the incident rays; I_x is the intensity of rays passing through a layer with thickness x ; and e is the base of the natural logarithms. In order to simplify the dependence of the attenuation coefficient upon the chemical nature of the material, μ can be expressed in terms of the density of the material ρ . Then, equation (1) takes the form

$$I_x = I_0 e^{-\rho k x}, \quad (2)$$

where k is a generalized coefficient for the linear absorption of the x-ray beams. It follows from equation (2) that, for fixed values of I_0 , k , and x , the attenuation of the intensity of x rays will depend upon one quantity only, the density of the material ρ [3].

One of the first methods of x-ray flaw inspection for the investigation of geological objects was used by V. K. Hamblin [8] while investigating the dependence between the degree of darkening of photoemulsions and the material compositions of layers possessing different absorption coefficients. N. A. Rukavina [11] showed that the intensity of the absorption of x rays by bottom sediments is also determined by the physical properties of the sediments (moisture content, density), the grain-size composition, and the content of organic matter.

The use of the method revealed a broad distribution of textures of various origins within visually homogeneous sediments and rocks [9, 10]; this attracted the attention of many investigators.

Odessa State University. Translated from *Litologiya i Poleznye Iskopaemye*, No. 4, pp. 131-136, July-August, 1989. Original article submitted June 7, 1988.

TABLE 1. Characteristics of the Composition and Properties of Investigated Samples of Mud Sediments

Station location	Depth of water table, m	Test interval, m	Origin and designation of sediments	Grain-size composition (make-up of fractions, %)				Mineral composition (fractions < 0.005, %)	Physical properties		
				< 1	1-0.05	0.05-0.005	<0.005		inherent moisture content W_n , %	density γ_0 , g/cm ³	porosity, n, %
Northwestern Prichernomor'e, Tiligul'skii liman	5.3	0.8-0.9	Liman silty mud	—	26.7	50.0	23.3	Hydromica (55), mixed-layer mica-montmorillonite (30), chlorite (10), kaolinite + hallousite (5)	48.8	1.66	61.6
Northwestern shelf of the Black Sea, Karkinit Bay	28.0	0.11-0.17	Marine pelitic mud	4.5	0.4		95.1	Hydromica (45), mixed-layer mica-montmorillonite (36), chlorite + kaolinite (19)	134.4	1.43	77.3
Pacific Ocean, region adjacent to the southeastern tip of the Kamchatka Peninsula	862.0	0.25-0.35	Marine, inequigranular sandy mud	11.92	38.19	22.15	27.64	Montmorillonite (60), hydromica (24), halloyside + kaolinite (18)	56.1	1.68	60.0
	908.0	1.29-1.36	Marine pelitic mud	2.98	16.32	26.72	53.98		76.4	1.53	66.8

Note. The grain-size composition and physical properties were determined according to standard methodologies at the soil laboratory of Odessa State University (the analyst was L. T. Zyryanova); the analysis of < 0.005-mm fraction was carried out at the mineralogical laboratory of Moscow State University under the direction of V. G. Shlykov.

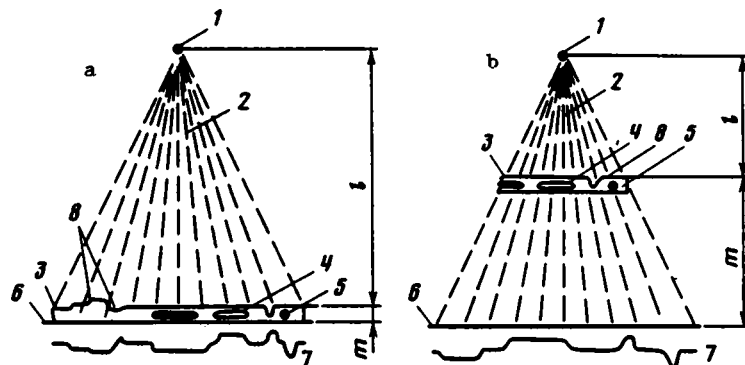


Fig. 1. Diagram of geometric conditions for radiographic inspection of an inhomogeneous object and a projection diagram of the darkening of the photoemulsions during the use of contact radiography (a) and microradiography (b): 1) emission source; 2) x rays; 3) object; 4) cavity; 5) inclusion; 6) film; 7) projection diagram of darkening; 8) relief associated with the surface of the object.

A. K. Larionov, V. F. Semenov [3], and A. X. Bouma [7] proposed optimal radiographic-photographic regimes for different types of rocks and sediments. However, the parametric conditions for radiographic analysis presented in the publications just mentioned were developed either in connection with foreign radiographic technology which we have no experience with or in connection with a wide-format apparatus giving a shadowy picture with vaguely outlined borders [6].

The nonuniform absorption of x rays by different parts of the object being inspected allows us to characterize the fluctuation in x-ray (physical) density associated with the object, i.e., allows us to detect inhomogeneities in the structure of the object. The detectability of structural elements within an object depends upon the type of emission source used, the geometric conditions present, the inspection regime, the photomaterials, and also the thickness and density of the object [4].

The optical properties of x-ray tubes used in modern instrumentation are determined by the dimensions of the tube's optical focal point [4], since the resolving power of the emission source and the width of the region of border blurring associated with a direct-shadow image depends upon the diameter of the focal point. One of the conditions for obtaining high-quality x-ray photographs is a minimal size for the tube's focal point. The miniature sharp-focus URS-0.02 x-ray apparatus with a focal point of $40 \pm 20\text{-}\mu\text{m}$ diameter complies with this requirement.

The geometric conditions (Fig. 1) associated with the inspection are determined by the distance from the emission source to the object l and the distance from the object to the photographic film m . The values of l and m can vary over a fairly significant range (from parts of a millimeter to tens of centimeters), depending upon the character of the object and the test before the investigation. Two modifications of the method under discussion can be distinguished in this respect. They are contact radiography and microradiography [7].

A peculiarity of the method of contact radiography is the critically small ($\ll 1\text{ mm}$) value of m . The value of l can be determined experimentally and usually amounts to 30-50 cm. The dimensions obtained for the image on the x-ray film coincides with the size of the object itself. The detail sensitivity of the method, determined with the aid of a standard [7] for mud samples 3 mm thick, amounts to approximately 2%. This means that the limiting size of inhomogeneities in the structure of a sample detectable on roentgenograms does not exceed $50\text{ }\mu\text{m}$.

In microradiography, the emission source is used as a x-ray shadow microscope. By placing the object of investigation at a short distance from the focal point of the tube and at a fairly large distance from the photographic film, one can obtain a definite magnification of the object M determined by the formula $M = (l + m)/l$. There is an optimal useful magnifi-

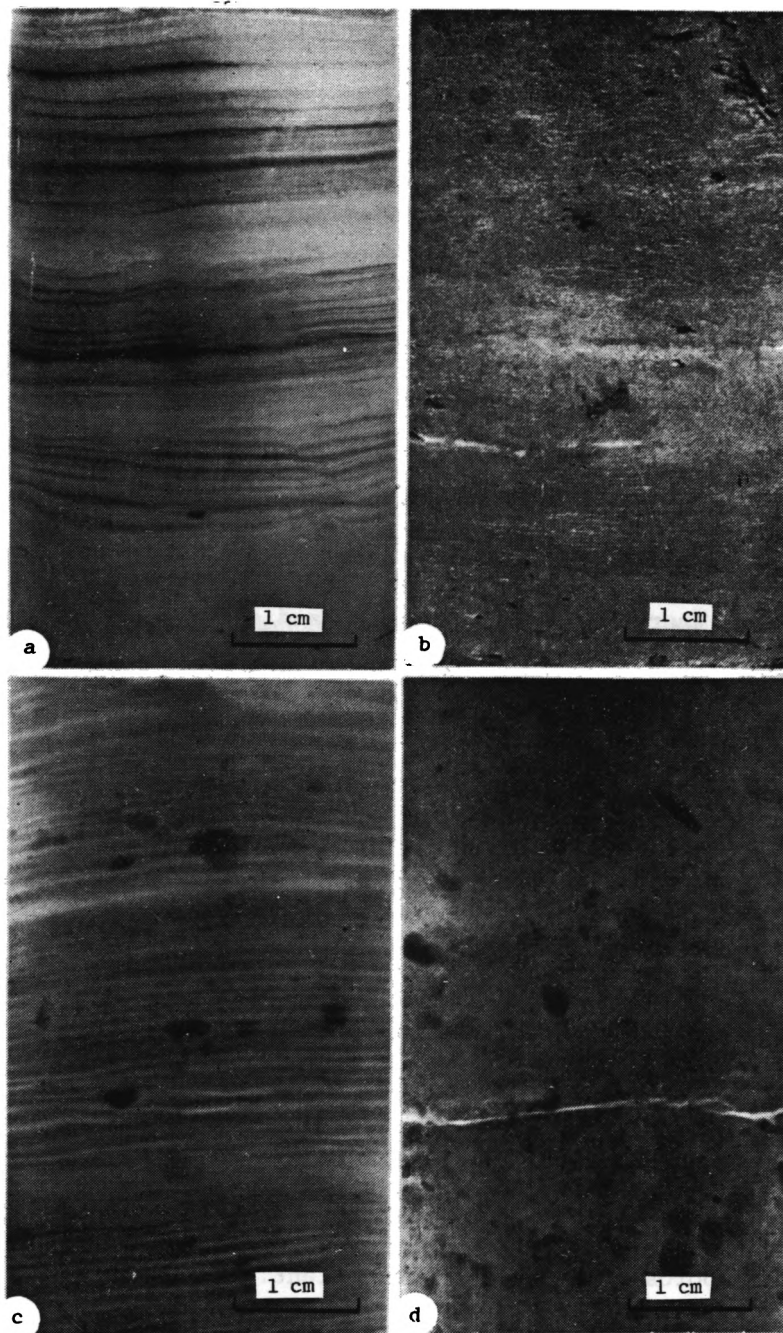


Fig. 2. Radiographic images (positives) of sediments of various origin. a) mud, horizontally parallel-layered [layering due to an alternation of thinner clayey-silty, optically denser clayey-carbonate, and clayey layers. Tiligul'skii liman]; b) photograph of the surface of the same sample; c) turbidite with parallel-layered texture and gravel inclusions [Pacific Ocean, depth of 908 m]; d) fluxoturbidite [layered and gradational textures absent; gravel fragments buried in finer matrix; Pacific Ocean, depth of 862 m].

cation; if this magnification is exceeded, a decrease in the sharpness of the image results. The useful magnification M_u is determined by the resolving power of the emission source and the ratio associated with it

$$M_u = k/\sigma,$$

where k is the resolving power of the normal eye, equal to 0.2 mm, σ is the least resolvable distance (within the object), corresponding to the diameter of the focal point [6] it follows from the equations presented that M_u does not exceed 5 when using the URS-0.02 apparatus.

As indicated by our investigations of the Upper Pleistocene-Holocene sediments of the shelf of the Black Sea, the limans of Prichernomor'ya, and the continental slope of the Pacific Ocean in the region of Kamchatka, the method of radiography can be successfully used to investigate the textural features of muds from various origins. Examples of photomages of individual samples are presented in Fig. 2, information concerning the composition and properties of these samples is presented in Table 1.

In accordance with the methodology described by A. X. Bouma [7] and modified somewhat by the authors of the present article, a thin string of plane-parallel sheets 0.3 cm thick and 6×10 cm in size are cut from a column of sediments with undisturbed structure and natural moisture content. The plates are then inspected by means of x-ray on the URS-0.02 apparatus. It should be noted that during the cutting of the plates from the monolith in cases involving a content of detritus-shelly material greater than 15%, deformation and breakage of the latter take place. Therefore, muddy coquinas and shelly muds are sampled with coring tubes up to 40 mm in diameter. The core material is directly transferred from the insert to cardboard capsules and are inspected whole on the more powerful RUP-12-5.2 x-ray apparatus. The recording of the images is carried out with the aid of photoplates used for nuclear investigations or double-sided PM-1 x-ray film.

In order to obtain comparable results between parallel determinations, the experimentally selected photography regimes on the URS-0.02 ($U = 25$ kV; $I = 250$ μ A; $t = 3$ min; $l + m = 35$ cm) and also the conditions for processing the photomaterials were standardized.

The combining of x-ray magnification with photomagnification allowed us to obtain an image of an object under investigation (or an image of an portion of such an object) over a wide range of magnifications, from 5 to 50. This is quite satisfactory for the visualization of textures at the macro- and meso-levels. To obtain greater magnifications, microfocus tubes with $\sigma = 1$ μ m can be used in combination with fine-grained PT-3 and PT-4 x-ray film.

Since the mineral composition of the clayey fraction in the investigated deposits of the northwestern shelf of the Black Sea are characterized by relatively constancy [2], attenuation of the intensities of x rays when the rays are passed through material from this area will be primarily determined by density of layering of this fraction. In turn, this allows us to recommend using the most common grain-size types of dispersed bottom sediments to carry out regional investigations for density standards. The methodology for preparing such standards consists in compressional sealing of samples (pastes) with given characteristics with respect to physical properties and texture, with subsequent laboratory control of their changes in density, porosity, and moisture content. The compacting loads are selected so that the individual prepared samples comprise a sequential, stepwise set, a density key with indices of physical characteristics comparable with analogous characteristics of sediments from the actual section under study and density gradient within the limits of 0.05-0.1 g/cm³.

In order to obtain a quantitative assessment of the changes in sample density on the basis of the degree of darkening of the x-ray film, a micrometer with appropriate technical characteristics is used [3].

Use of the radiographic method [1] has allowed researchers to discover the widespread occurrence of textures of various origins within sediments, to obtain a characterization of the relative frequency of occurrence of various textures and their combinations within different sedimentary environments, and to discover the high lateral variability of shelf sediments with respect to texture.

The advantages of the radiography method which we have enumerated above confirm the advisability of widespread use of this method, both under stationary conditions and on ship-board laboratories.

LITERATURE CITED

1. V. M. Voskoboinikov, B. I. Krakovskii, E. G. Konikov, and V. V. Yanko, "Textures of bottom sediments," in: The Geology of the Shelf of the Ukrainian SSR. Lithology, Nauka Dumka, Kiev (1985), pp. 130-138.
2. B. I. Krakovskii, "An association of clay minerals and their distribution within the Holocene sediments on the northwestern portion of the shelf of the Black Sea," Geol. Zh., 42, No. 6, 102-107 (1982).
3. A. K. Larionov and V. F. Semenov, "Investigation of the density and structure of soils by the method of radiography," Tr. Voronezhskova Inzhenerno-Stroitel. Inst., 10, No. 2, 49-63 (1965).
4. S. V. Rumyantsev, "X-Ray Flaw Detection [in Russian], Atomizdat, Moscow (1974).
5. G. N. Flerov and I. G. Berezina, "Radiography of Minerals in Rocks and Ores [in Russian], Atomizdat, Moscow (1979).
6. F. N. Kharabzha, General Course in X-Ray Technology [in Russian], Gosénergoizdat, Moscow, Leningrad (1960).
7. A. X. Bouma, Methods for the Study of Sedimentary Structures, Wiley Interscience, N.Y. (1969).
8. W. K. Hamblin, "X-ray radiography in the study of structures in homogeneous sediments," J. Sediment. Petrol., 32, No. 2, 201-210 (1962).
9. W. K. Hamblin, "Internal structures of 'homogeneous' sandstones," Bull. State Geol. Surv. Kans., 175, (1965).
10. H. E. Kane, "Minor internal sedimentary structures in core sediments of Sabine Lake and adjacent water bodies, Texas-Louisiana," J. Sediment. Petrol., 34, 419-421 (1964).
11. N. A. Rukavina, "Rapid inspection of soft sediment cores by x-radiography," Proc. 10th Conf. Great Lakes Resources, Toronto (1967). pp. 143-148.

ПЕРЕВОДЧИКИ!

FOR RUSSIAN-ENGLISH SCIENTIFIC AND TECHNICAL TRANSLATIONS

You can follow the latest Soviet research in your field, and supplement your income, by translating in your home on a free-lance basis. If you have a good command of English, a good knowledge of Russian, and experience or academic training in a scientific or technical discipline, you may be qualified for our translation program. Immediate openings are available in chemistry, biology, medicine, physics, mathematics, materials science, and biomedical, environmental, and chemical engineering, as well as other fields.

For additional information write or call:

Translations Editor
Plenum Publishing Corporation
233 Spring Street, New York, N.Y. 10013, USA
Tel. (212) 620-8441

CHANGING YOUR ADDRESS?

In order to receive your journal without interruption, please complete this change of address notice and forward to the Publisher, 60 days in advance, if possible.

(Please Print)

Old Address:

name

address

city

state (or country)

zip code

New Address

name

address

city

state (or country)

zip code

date new address effective

name of journal

THE LANGUAGE OF SCIENCE
Plenum
PUBLISHING CORPORATION

233 Spring Street, New York, New York 10013

MECHANICS OF COMPOSITE MATERIALS*Mekhanika Kompozitnykh Materialov*

Vol. 26, 1990 (6 issues) \$745

MELTS*Rasplavy*

Vol. 4, 1990 (6 issues) \$295

METAL SCIENCE AND HEAT TREATMENT*Metallovedenie i Termicheskaya Obrabotka Metallov*

Vol. 32, 1990 (12 issues) \$915

METALLURGIST*Metallurg*

Vol. 34, 1990 (12 issues) \$915

PROBLEMS OF INFORMATION TRANSMISSION*Problemy Peredachi Informatsii*

Vol. 26, 1990 (4 issues) \$695

PROGRAMMING AND COMPUTER SOFTWARE*Programmirovaniye*

Vol. 16, 1990 (6 issues) \$395

PROTECTION OF METALS*Zashchita Metallov*

Vol. 26, 1990 (6 issues) \$915

RADIOPHYSICS AND QUANTUM ELECTRONICS*Izvestiya Vysshikh Uchebnykh Zavedenii, Radiofizika*

Vol. 33, 1990 (12 issues) \$915

REFRACTORIES*Ogneupory*

Vol. 31, 1990 (12 issues) \$815

SIBERIAN MATHEMATICAL JOURNAL*Sibirskii Matematicheskii Zhurnal*

Vol. 31, 1990 (6 issues) \$1045

**SOIL MECHANICS AND
FOUNDATION ENGINEERING***Osnovaniya, Fundamenty i Mekhanika Gruntov*

Vol. 27, 1990 (6 issues) \$815

SOLAR SYSTEM RESEARCH*Astronomicheskii Vestnik*

Vol. 24, 1990 (4 issues) \$615

SOVIET APPLIED MECHANICS*Prikladnaya Mekhanika*

Vol. 26, 1990 (12 issues) \$915

SOVIET ATOMIC ENERGY*Atomnaya Energiya*

Vols. 68-69, 1990 (12 issues) \$945

**SOVIET JOURNAL OF GLASS PHYSICS
AND CHEMISTRY***Fizika i Khimiya Stekla*

Vol. 16, 1990 (6 issues) \$515

**SOVIET JOURNAL OF
NONDESTRUCTIVE TESTING***Defektoskopiya*

Vol. 26, 1990 (12 issues) \$1045

SOVIET MATERIALS SCIENCE*Fiziko-khimicheskaya Mekhanika Materialov*

Vol. 26, 1990 (6 issues) \$815

SOVIET MICROELECTRONICS*Mikroelektronika*

Vol. 19, 1990 (6 issues) \$545

SOVIET MINING SCIENCE*Fiziko-tehnicheskie Problemy Razrabotki**Poleznykh Iskopaemykh*

Vol. 26, 1990 (6 issues) \$855

SOVIET PHYSICS JOURNAL*Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika*

Vol. 33, 1990 (12 issues) \$915

**SOVIET POWDER METALLURGY AND
METAL CERAMICS***Poroshkovaya Metallurgiya*

Vol. 29, 1990 (12 issues) \$945

STRENGTH OF MATERIALS*Problemy Prochnosti*

Vol. 22, 1990 (12 issues) \$1045

THEORETICAL AND MATHEMATICAL PHYSICS*Teoreticheskaya i Matematicheskaya Fizika*

Vols. 82-85, 1990 (12 issues) \$895

UKRAINIAN MATHEMATICAL JOURNAL*Ukrainskii Matematicheskii Zhurnal*

Vol. 42, 1990 (12 issues) \$995

Send for Your Free Examination Copy**Plenum Publishing Corporation, 233 Spring St., New York, N.Y. 10013**
In United Kingdom: 88/90 Middlesex St., London E1 7EZ, England

Prices slightly higher outside the U.S. Prices subject to change without notice.

RUSSIAN JOURNALS IN THE PHYSICAL AND MATHEMATICAL SCIENCES

AVAILABLE IN ENGLISH TRANSLATION

ALGEBRA AND LOGIC

Algebra i Logika

Vol. 29, 1990 (6 issues) \$635

ASTROPHYSICS

Astrofizika

Vols. 32-33, 1990 (6 issues) \$745

AUTOMATION AND REMOTE CONTROL

Avtomatika i Telemekhanika

Vol. 51, 1990 (24 issues) \$1045

COMBUSTION, EXPLOSION, AND SHOCK WAVES

Fizika Goreniya i Vzryva

Vol. 26, 1990 (6 issues) \$815

COMPUTATIONAL MATHEMATICS AND MODELING

A translation of selected works in mathematics

Vol. 1, 1990 (4 issues) \$295

COSMIC RESEARCH

Kosmicheskie Issledovaniya

Vol. 28, 1990 (6 issues) \$915

CYBERNETICS

Kibernetika

Vol. 26, 1990 (6 issues) \$815

DIFFERENTIAL EQUATIONS

Differentsial'nye Uravneniya

Vol. 26, 1990 (12 issues) \$915

DOKLADY BIOPHYSICS

Doklady Akademii Nauk SSSR

Vols. 310-315, 1990 (2 issues) \$275

FLUID DYNAMICS

Izvestiya Akademii Nauk SSSR.

Mekhanika Zhidkosti i Gaza

Vol. 25, 1990 (6 issues) \$915

FUNCTIONAL ANALYSIS AND ITS APPLICATIONS

Funktsional'nyi Analiz i Ego Prilozheniya

Vol. 24, 1990 (4 issues) \$695

GLASS AND CERAMICS

Steklo i Keramika

Vol. 47, 1990 (12 issues) \$945

HIGH TEMPERATURE

Teplofizika Vysokikh Temperatur

Vol. 28, 1990 (6 issues) \$915

HYDROTECHNICAL CONSTRUCTION

Gidrotekhnicheskoe Stroitel'stvo

Vol. 24, 1990 (12 issues) \$695

INDUSTRIAL LABORATORY

Zavodskaya Laboratoriya

Vol. 56, 1990 (12 issues) \$915

INSTRUMENTS AND EXPERIMENTAL TECHNIQUES

Pribory i Tekhnika Eksperimenta

Vol. 33, 1990 (12 issues) \$1015

JOURNAL OF APPLIED MECHANICS AND TECHNICAL PHYSICS

Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki

Vol. 31, 1990 (6 issues) \$915

JOURNAL OF APPLIED SPECTROSCOPY

Zhurnal Prikladnoi Spektroskopii

Vols. 52-53, 1990 (12 issues) \$935

JOURNAL OF ENGINEERING PHYSICS

Inzhenerno-fizicheskii Zhurnal

Vols. 58-59, 1990 (12 issues) \$935

JOURNAL OF SOVIET LASER RESEARCH

A translation of articles based on the best

Soviet research in the field of lasers

Vol. 11, 1990 (6 issues) \$395

JOURNAL OF SOVIET MATHEMATICS

*A translation of selected Russian works
in mathematics*

Vols. 48-52, 1990 (30 issues) \$2250

LITHOLOGY AND MINERAL RESOURCES

Litologiya i Poleznye Iskopaemye

Vol. 25, 1990 (6 issues) \$915

LITHUANIAN MATHEMATICAL JOURNAL

Litovskii Matematicheskii Sbornik

Vol. 30, 1990 (4 issues) \$545

MAGNETOHYDRODYNAMICS

Magnitnaya Gidrodinamika

Vol. 26, 1990 (4 issues) \$695

MATHEMATICAL NOTES

Matematicheskie Zametki

Vols. 47-48, 1990 (12 issues) \$915

MEASUREMENT TECHNIQUES

Izmeritel'naya Tekhnika

Vol. 33, 1990 (12 issues) \$915

continued on inside back cover